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1916-1917 TO 1919-1920

A

FROM THE DEPARTMENTS OF MATHEMATICS, PHYSICS, CHEMISTRY AND ENGINEERING.

For Private Circulation only.

SYDNEY, 1920.

This volume only contains copies of those papers of which special reprints were available, and does not represent the whole of the published work contributed during the stated period by the departments specified on the title page. By way of index a complete list is given herewith of the published work of the departments of Mathematics, Physics, Chemistry and Engineering during the period 1916-17 to 1919-20. The papers marked with an asterisk are included in the present volume. Papers marked with a double asterisk were accidentally omitted from the index of the previous volume.

MATHEMATICS.

H. S. CARSLAW, M.A., Sc.D. (Camb.), D.Sc (Glasgow) F.R.S.E.

Professor of Mathematics Pure and Applied.

**1. Plane trigonometry: an elementary text-book for the higher classes of secondary schools and for colleges. [Second ed., with corrections.] London, Macmillan and Co., Ltd., 1915, 8vo., pp. xviii, 293, i, xii.

**2. Solutions of the questions in plane trigonometry. London, Macmillan & Co., Ltd., 1915, 8vo. [With Miss F. Cohen, M.A., B.Sc.].

**3. The discovery of logarithms by Napier. *Math. Gaz.*, May 1915, viii, no. 117, pp. 76-84. July, no. 118, pp. 115-119.

 4. Easy numerical trigonometry of the right-angled triangle. Sydney 1916, 8vo., pp. 96, 2.

 5. Easy numerical trigonometry. Sydney, 1916, 8vo., p. 142.

*6. A progressive income tax. *Math. Gaz.*, May 1916, viii, no. 123, pp. 253-258.

*7. Napier's logarithms: the development of his theory. *Jour. and Proc. Roy. Soc. N.S.W.*, 1916, pp. 130-142.

 7a ― ‐‐ *Phil. Mag.*, Nov. 1916, xxxii, no. 191 pp. 476-486.

 8. Napier's logarithmic concept. *Amer. Math. Monthly.* Oct. 1916, xxiii, no 8, pp. 310-312.

 9 Elements of non-euclidian plane geometry and trigonometry (Longman's modern mathematical series). London, 1916, 8vo. Pp. xii, 179, 116 diagrams.

*10. A trigonometrical sum and the Gibbs phenomenon in Fourier's series. *Amer. Jour Math.*, Apr. 1917, xxxix, no. 2, pp. 185-198.

*11. The Green s function for the equation $\Delta^3 u + \kappa^2 = 0$; second paper *Proc. Lond. Math. Soc.*, 1917, 2nd ser., xvi, pt. 2, pp. 84-93.

 12. A progressive income tax. *Math. Gaz.*, Oct. 1917, ix, no. 131, pp. 137-138

 13. A simple progressive tax and its bearing on the Federal Income Tax and other Acts. *Jour. and Proc. Roy. Soc. N.S.W.*, 1918, lii, pp. 203 214.

*14. Diffraction of waves by a wedge of any angle. *Proc. Lond. Math. Soc.* 1919, 2nd ser, xviii, pt. 4, pp. 291-307, fig.1-5.

*15. Bromwich's method of solving problems in the conduction of heat. *Phil. Mag.*, May 1920, xxxix, pp. 603-610.

E. M. WELLISCH, M.A. (Syd), B.A (Cantab.)

Lecturer in Applied Mathematics.

 1. Free electrons in gases. *Phil. Mag.*, March 1916, xxxi. pp. 186-189.

 2. The motion of ions and electrons through gases. *Phil. Mag*, July 1917, xxxiv, pp. 33-36.

 2a. ‐‐‐‐‐‐ *Amer. Jour. Sci.*, July 1917, xliv, no. 259 (whole no. 194), pp 1 32.

PHYSICS.

J. A. POLLOCK, D.Sc, F.RS.

Professor of Physics.

 1. Practical physics; 2nd edition, revised and enlarged. Sydney, 1918, 8vo. Pp. xi, 164 [With O. U. Vonwiller.]

*2. A note on a relation between the thermal conductivity and the viscosity of gases. *Jour. and Proc. Roy. Soc. N.S.W.* 1919, liii, pp. 116-119.

EDNA D. SAYCE, B.Sc.

Demonstrator in Physics, 1917-18.

*1. Some determinations of the heat conductivity of selenium. *Jour. and Proc. Roy. Soc. N.S.W.*, 1917, li, pp. 356-363.

O. U. VONWILLER, B.Sc.

Assistant Professor of Physics.

 1. *See* J. A. Pollock (1).

*2. Notes on the elastic properties of selenium. *Jour. and Proc. Roy. Soc. N.S.W.*, 1919, liii, pp. 136-143.

CHEMISTRY.

Janet F. McGillivray Brown, B.A., B.Sc.

Science Research Scholar 1915.

1. *See* R Robinson (7).

G. J. Burrows, B.Sc.

Lecturer and Demonstrator in Chemistry.

*1. Volume changes in the process of solution. *Jour. and Proc. Roy. Soc. N.S.W.*, 1919, liii, pp. 74-99.
*2. On the hydrolysis of urea hydrochloride. *Jour. and Proc. Roy. Soc. N.S.W.*, 1919, liii, pp. 125-135.
3. The rate of hydrolysis of methyl acetate by hydrochloric acid in water acetone mixtures. *Jour. Chem. Soc., Trans.*, Nov. 1919, cxv, no. 685, pp. 1230-1239.
4. The constitution of the nitroprussides. Part 1. Conductivity and cryoscopic measurements. *Jour. Chem. Soc., Trans.*, Dec. 1919, cxv, no. 686, pp. 1429-1435. [With E. E. Turner.]

C. E. Fawsitt, D.Sc. (Edin.), Ph.D. (Leip.)

Professor of Chemistry.

*1. Cineol as a solvent in cryoscopy. *Jour. and Proc. Roy. Soc. N.S.W.*, 1917, li, pp. 467-472. [With C. H. Fischer.]
*2. Experiments on the behaviour of iron in contact with sulphuric acid. *Jour. and Proc. Roy. Soc. N.SW.*, 1918, lii, pp. 396-404. [With A. A. Pain.]
3. The freezing point of solutions, with special reference to solutions containing several solutes. *Jour. Chem. Soc.*, July 1919, cxvi, no. 681, pp. 790-801.
4. The use of freezing point determinations in quantitative analyses. *Jour. Chem. Soc.*, July 1919, cxvi, no. 681, pp. 801-808.
5. Presidential address, delivered before the Royal Society, N.S.W., Dec. 3rd 1919. Pp. 24, roy. 8vo. Sydney, 1920. [To appear in *Jour. and Proc. Roy. Soc. N.S.W.*, 1920, liv, pp. 1-24.]
*6. The miscibility of liquids. *Jour. and Proc. Roy. Soc. N.S.W.*, 1919, liii, pp. 162-165. [With C. H. Fischer.]

C. H. Fischer.

1. *See* C. E. Fawsitt (1).
2. *See* C. E. Fawsitt (6).

J. G. Stephens, B.Sc.

John Coutts Scholar, 1919.

*1. A new method of measuring molecular weights. *Jour. and Proc. Roy. Soc. N.S.W.*, 1919, liii, pp. 166-170, 1 fig.

Ellice E. P. Hamilton, B.A., B.Sc.

Science Research Scholar, 1915.

1. *See* R. Robinson, (2).

G. Harker, B.Sc. (Syd.), D.Sc. (Lond.)

Lecturer and Demonstrator in Organic Chemistry, Pure and Applied.

*1. The analysis of toluene and benzine in coal tar oils. *Jour. and Proc. Roy. Soc. N.S.W.*, 1916, pp. 99-105
*2. Macrozamia Spiralis as a source of industrial alcohol. *Science and Industry : Official journal of the Commonwealth Institute of Science and Industry*, Dec. 1919, i, no. 8, pp. 470-475.
3. Note on explosions in coal mines. *Jour. Soc. Chem. Ind.*, 15 Dec. 1919, xxxviii, no. 17, p. 388.
4. Starch from Lamia palm. *Science and Industry : Official journal of the Commonwealth Institute of Science and Industry*, Jan 1920, ii, no. 1, pp. 37.

ELLEN M. HINDMARSH, B.Sc.

Demonstrator in Physiology

1. *See* R. Robinson (4).

T. G. H. JONES, B.Sc.

Science Research Scholar, 1915.

1. *See* R. Robinson (3).

ANNIE M. B. ORR, B.Sc.

Caird Scholar, 1915.

1. *See* R. Robinson (5)

JOHN READ, M.A., (Camb.), Ph.D. (Zurich), B.Sc. (Lond.).

Professor of Organic Chemistry, Pure and Applied.

1. The action of bromine water on ethylene. *Jour Chem. Soc., Trans.*, April 1917, cxi, no. 654, pp. 240-244. [With M. M. Williams.]
*2. A novel application of bromine water in synthetic organic chemistry. *Jour and Proc. Roy. Soc. N.S.W.*, 1917, li, pp. 558-564. [With M. M. Williams]
*3. Note on a Papuan natural petroleum, *Jour. Soc. Chem. Ind.*, 30 Aug. 1919, xxxviii, pp. 310-312. [With M. M. Williams.]
*4. An investigation of the " marine fibre " of Posidonia australis. *Commonwealth of Aus. Inst. of Sci. and Industry Bulletin*, 1919, no. 14, pp. 60, 20 plates. [With H G. Smith.]
*5. The preparation of Halogenohydrins. *Jour. Chem. Soc., Trans.*, April 1920, cxvii, no. 690, pp. 359-362. [With M. M. Williams.]

ROBERT ROBINSON, D.Sc.

Professor of Pure and Applied Organic Chemistry, 1913-1915.

**1. A decomposition of certain o-nitromandelic acids. *Jour. Chem. Soc., Trans.*, 1915, cvii, pt. 2, pp. 1753-1762. [With G. M. Robinson.]
2. An extension of the theory of addition to conjugated unsaturated systems Part I. Note on the constitution of the salts of 1 benzylidene—2 methyl 1 : 2 : 3 : 4 tetra hydroisoquinoline. *Jour. Chem. Soc., Trans.*, Oct. 1916, cix, pt. 2, no. 648, pp. 1029-1038. [With E. E. P. Hamilton. Work done at Sydney and Liverpool Universities.]
3. Experiments on the orientation of substituted catechol ethers. *Jour. Chem. Soc., Trans.*, Oct. 1917, cxi, pt. 2, no. 660, pp. 903-929. [With T. G H Jones. Work done at University of Sydney.]
4. 5-bromoguaiacol and some derivatives. *Jour. Chem. Soc., Trans.*, Oct. 1917, cxi, pt. 2, no. 660, pp. 940-946. [With E. M. Hindmarsh and J. Knight. Work done at University of Sydney.]
5. The action of halogens on piperonal. *Jour Chem. Soc., Trans.*, Oct. 1917, cxi, pt. 2, no. 660, pp. 946-952. [With A. M. B. Orr and M. M. Williams. Work done at University of Sydney.]
6. Researches on pseudo-bases. Part II. Note on some berberine derivatives and remarks on the mechanism of the condensation reactions of pseudo bases. *Jour. Chem. Soc., Trans.*, Oct. 1917, cxi, pt. 2, no. 660, pp. 958-969. [With G. M. Robinson. Work done at Sydney and Liverpool Universities.]
7. Veratricsulphinide. *Jour. Chem. Soc., Trans.*, Oct. 1917, cxi, no. 660, pp. 952-958. [With J. F. McG. Brown. Work done at University of Sydney.]

GERTRUDE M. ROBINSON, M.Sc.

Demonstrator in Organic Chemistry, 1913-1914.

1. A reaction of homopiperonyl and of homoveratryl alcohols. *Jour. Chem. Soc., Trans.*, 1915, cvii, pt. i, pp. 267-276. [Work done at Sydney University.]
2. Experiments on the so called migrations of atoms and groups. Part I. The nitration of p-iodo-anisole and other iodophenolic ethers. *Jour. Chem. Soc., Trans.*, Oct. 1916, cix, pt. 2, no. 648, pp. 1078-1091. [Work done at Sydney and Liverpool Universities.]
3. Azoxycatechol ethers and related substances. *Jour. Chem. Soc., Trans.*, Feb. 1917, cxi, pt. 1, no. 652, pp. 109 121. [Work done at Sydney and Liverpool Universities.]
4. *See* R. Robinson (6).

E. E. TURNER, B.A., M.Sc., A.I.C.

Lecturer and Demonstrator in Organic Chemistry, Pure and Applied.

*1 Note on organo-metallic derivatives of chromium tungsten and iron. *Jour. and Proc. Roy. Soc. N.S.W.,* 1919, liii, pp. 100 101. [With G. M. Bennett.]

2. *See* G. J. Burrows (4).

*3. The action of cupric chloride on organo-metallic derivatives of magnesium. *Jour. and Proc. Roy. Soc. N.S.W.,* 1920, liv, pp. 37-39.

MARGARET M. WILLIAMS, B.Sc.

Science Research Scholar, 1916. Demonstrator in Organic Chemistry, 1917.

1. *See* J. Read (1).

2. *See* R. Robinson (6).

3. *See* J. Read (2).

4. *See* J. Read (4).

5. *See* J. Read (6).

ENGINEERING.

Sir HENRY BARRACLOUGH K.B.E., B.E. (Syd.), M.M.E. (Cornell), Assoc. M. Inst. C.E., M.I.Mech.E.

Professor of Mechanical Engineering.

1. Military field engineering. *Proc. Eng. Assoc. N.S.W.,* 1914-1915, xxx, pp. 1-8.

J. P. V. MADSEN, B.Sc., B.E. (Syd.), D.Sc. (Adelaide)

Professor of Electrical Engineering.

*1. Preliminary account of a magneto extensometer. *Jour. of Proc. of the Electrical Association of Australia, N.S.W.,* 1920, iv, pp. 1-20.

E. P. TAYLOR, B.E.

Science Research Scholar 1912. Hall Fellow in Engineering, 1915

1. Carburettor action. *Jour. and Proc. Syd. Univ. Eng. Soc.,* 1915-16 and 1916-17, 1918, xx, pp. 75-94, 6 figs.

A PROGRESSIVE INCOME-TAX.

By Professor H. S. Carslaw.

In this paper I propose to describe a scheme of progressive taxation which has been introduced in Australia in the "Income-Tax Act, 1915" (Commonwealth of Australia). As a novel illustration of the use of the Integral Calculus it may be of interest to readers of the *Mathematical Gazette*. Incidentally I desire to point out the need for care in using the term "rate of tax" when such a progressive tax is described. In the schedules of this Act the words are used in at least two different senses. And if the curves of the second degree, or any degree, are to be referred to in Acts of Parliament—a step the wisdom of which certainly may be questioned so long as the mathematical knowledge of the average man remains what it is—the nature of the curves might with advantage be more clearly stated than is done in this Act.

To take the simplest possible case of a progressive tax, let us suppose the tax arranged as follows:

On the 1st pound, the tax is $(a + \frac{1}{2}b)$ pence

On the 2nd pound, the tax is $(a + \frac{3}{2}b)$ pence

....

On the nth pound, the tax is $\left(a + \frac{2n-1}{2}b\right)$ pence.

Then on £n the tax will be got by summing this Arithmetical Progression, and we have for the result $n(a + \frac{1}{2}nb)$ pence. We might say that the rate per £ on an income of £n is $(a + \frac{1}{2}nb)$ pence. However, this way of describing the tax would be unfortunate. It does not distinguish between the *rate at the nth pound* and the *average rate on* £n.

The change in the rate of the tax in this example has taken place at each increment of £1. It might have taken place continuously, just as Compound Interest can be reckoned from instant to instant, instead of yearly, half-yearly, or quarterly. Modifying the example, we shall assume that the rate in pence at the xth pound is given by the equation

$$R = a + bx.$$

Then the tax on £x would be $\int_0^x (a + bx)dx$ pence, or $x(a + \frac{1}{2}bx)$ pence.

It is interesting to examine these two cases graphically. Taking two rectangular axes, let the x-axis refer to sums in pounds sterling and the R-axis to rates in pence.
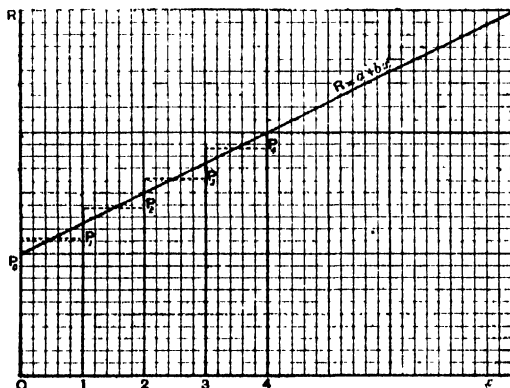
In the figure, the line $R = a + bx$

is drawn, and the ordinates at the points on the axis of x, whose abscissae are 1, 2, 3, etc., meet this line at P_1, P_2, P_3, etc.

The tax on the nth pound in the second example is given by the area of the trapezium whose top corners are P_{n-1} and P_n.

The dotted lines in the figure, through the middle points of P_0P_1, P_1P_2, etc., are at distances $a + \frac{1}{2}b$, $a + \frac{3}{2}b$, etc., from the axis of x. And the areas of the successive rectangles which we thus introduce into this figure give the tax on the successive pounds in the first example.

It will be seen that the tax on £n in these two cases is the same. And it should be noted that though the rate of the tax at the nth pound is $(a + bn)$, the tax on the nth pound is $\left(a + \frac{2n-1}{2} b\right)$. The distinction here referred to corresponds to that which meets the beginner when he is dealing. with velocity in a straight line under constant acceleration. With the usual notation, the velocity at the time t is given by $V + ft$, and the distance travelled in the interval $(t, t+1)$ is $V + f(t + \frac{1}{2})$.

When the rate of tax at the xth pound is given by the equation

$$R = a + bx, \quad\quad\quad\quad\text{......................................(1)}$$

we might quite naturally say that the rate increases continuously in a curve of the first degree. And it is but a step to extend this to the cases

$$R = a_0 + a_1x + a_2x^2 \quad\quad\text{......................................(2)}$$

and $$R = a_0 + a_1x + a_2x^2 + a_3x^3. \quad\quad\text{..............................(3)}$$

These are the curves of the second and third degrees introduced into the Income Tax Act, as will be seen below.

In (2), the tax for such part of a man's income as lies between £x_1 and £x_2 would be

$$\int_{x_1}^{x_2} (a_0 + a_1 x + a_2 x^2)\,dx,$$

and in (3) it would be

$$\int_{x_1}^{x_2} (a_0 + a_1 x + a_2 x^2 + a_3 x^3)\,dx.$$

Let us now turn to the Schedules of the Act. The First Schedule deals with Income from Personal Exertion. It reads as follows :

FIRST SCHEDULE.

Rate of Tax upon Income derived from Personal Exertion.

For so much of the taxable income* as does not exceed £7,600 the rate of tax per pound sterling shall be Threepence and three eight-hundredths of one penny where the taxable value is One pound sterling, and shall increase uniformly with each increase of One pound sterling of the taxable income by three eight-hundredths of one penny.

For every pound sterling of taxable income in excess of £7,600 the rate of tax shall be sixty pence.

The rate of tax for so much of the taxable income as does not exceed £7,600 may be calculated from the following formula :

$R =$ rate of tax in pence per pound sterling.

$I =$ taxable income in pounds sterling.

$$R = \left(3 + \frac{3}{800}\,I\right) \text{ pence.}$$

It will be noted that if we take the continuously progressive tax, the rate in pence at the xth pound in this case is given by the equation

$$R = 3 + \tfrac{3}{400}x,$$

and that, when $x = 7,600$, we have $R = 60$.

In this schedule it would have been more correct to say that

$$R = 3 + \tfrac{3}{800}I,$$

and that the tax on £I is $(3 + \tfrac{3}{800}I)I$ pence.

The "rate of tax" referred to in the schedule as R is the "average rate."

The Second Schedule deals with Income from Property. It reads as follows :

SECOND SCHEDULE.

Rate of Tax upon Income derived from Property.

(a) For income of a taxable value not exceeding £546 the rate of tax shall be calculated from the following formula :

$R =$ rate of tax in pence per pound sterling.

$I =$ taxable income in pounds sterling.

$$R = \left(3 + \frac{1}{181\cdot07}\right) \text{ pence.}$$

*The words "taxable income" are used because of deductions allowed in certain circumstances.

(b) For income of a taxable value exceeding £546 but not exceeding £2,000 the rate of tax shall be calculated in the following manner:

> The rate of the tax shall increase continuously with the increase of the taxable value of the income in a curve of the second degree in such a manner that the increment of tax per pound increase of taxable income shall be—

			Equivalent to an average rate of:—	Note.—Amount of tax for incomes of these amounts.
at a taxable income of	£546	11·713 pence	·015 pence	£546 - £13 13
at a taxable income of	£600	12·768 pence	·576 pence	£600 - 16 6
at a taxable income of	£700	14·672 pence	·597 pence	£700 - 22 3
at a taxable income of	£800	16·512 pence	·597 pence	£800 - 25 18
at a taxable income of	£900	18·288 pence	·576 pence	£900 - 35 18
at a taxable income of £1,000		20·000 pence	·533 pence	£1,000 - 43 17
at a taxable income of £1,500		27·600 pence	·000 pence	£1,500 - 93 15
at a taxable income of £2,000		33·600 pence	·933 pence	£2,000 - 157 15

(c) For income of a taxable value exceeding £2,000 the rate of tax shall be calculated in the following manner:

> For so much of taxable value as does not exceed £6,500, the rate of tax shall increase continuously with the increase of the taxable value of the income in a curve of the third degree in such a manner that the increment of tax per pound increase of taxable income shall be—

		Equivalent to an average rate of:—	Note.—Amount of tax for incomes of these amounts.
at a taxable income of £2,000	33·600 pence	18·9333 pence	£2,000 - £157
at a taxable income of £2,500	40·000 pence	22·5258 pence	£2,500 - 234
at a taxable income of £3,000	45·300 pence	25·8944 pence	£3,000 - 323
at a taxable income of £3,500	49·600 pence	28·9651 pence	£3,500 - 422
at a taxable income of £4,000	53·000 pence	31·7833 pence	£4,000 - 525
at a taxable income of £4,500	55·600 pence	34·2921 pence	£4,500 - 642
at a taxable income of £5,000	57·500 pence	36·5333 pence	£5,000 - 760
at a taxable income of £5,500	58·800 pence	38·4636 pence	£5,500 - 882
at a taxable income of £6,000	59·600 pence	40·2292 pence	£6,000 - ,005
at a taxable income of £6,500	60·000 pence	41·7306 pence	£6,500 - ,130

> For every pound sterling of taxable income in excess of £6,500 the rate of tax shall be sixty pence.

This is a somewhat terrifying document: and one sympathises with the Treasurer in the task of explaining it to the House. Indeed, when Mr. Hughes, apologizing for its obscurity, was informed by the Leader of the Opposition that he quite understood the whole matter, he replied that if this were so his friend was much more fortunate than himself.

In section (a), dealing with incomes not exceeding £546, we have another case of the formula

$$R = a + bx,$$

giving for the tax on £x the sum of $x(a + \tfrac{1}{2}bx)$ pence.

It will be noticed that it would have been more correct to say that the rate is given by

$$R = 3 + \frac{2}{181 \cdot 07} I,$$

and the tax on £I is $\left(3 + \dfrac{1}{181 \cdot 07} I\right) I$ pence.

Further, there is a discontinuity in the rate of tax in passing through £546 from (a) to (b).

In section (b) we meet the equation

$$R = a_0 + a_1 x + a_2 x^2.$$

It will be found by solving three linear equations that the "increments" for £1,000, £1,500 and £2,000 give the following values for a_0, a_1 and a_2:

$$a_0 = 0, \quad a_1 = \frac{23 \cdot 2}{10^3} \quad \text{and} \quad a_2 = -\frac{3 \cdot 2}{10^6}.$$

Also these values fit the "increments" for the other sums given in (b), except £546, where they give $11 \cdot 7132288$ instead of $11 \cdot 713$.

For the other incomes named the "increments" are exact: this one is correct to three places.

But it should be noted that when

$$R = a_0 + a_1 x + a_2 x^2,$$

the tax on the xth pound is $\int_{x-1}^{x} (a_0 + a_1 x + a_2 x^2) dx$, and in the wording of the schedule the "rate of tax" and the "increment" are confused. As a matter of fact "the increments of tax per pound increase of taxable income" are not as given in the Act.

In section (c), we meet the equation

$$R = a_0 + a_1 x + a_2 x^2 + a_3 x^3.$$

Taking the last four figures (£5,000 to £6,500) it will be found by solving four linear equations that the values for a_0, a_1, a_2 and a_3 are as follows:

$$a_0 = -5, \quad a_1 = \frac{25 \cdot 1\dot{6}}{10^3}, \quad a_2 = -\frac{3 \cdot 2}{10^6}, \quad a_3 = \frac{0 \cdot 1\dot{3}}{10^9}.$$

And these values fit the other "increments" exactly.

Though the wording of the schedule does not make this quite clear, the figures given in the Notes to (b) and (c) show that section (a) is to be used for the part of the income up to £546, (b) for the part from £546 to £2,000, and (c) for the part from £2,000 to £6,500.

And it would appear that the formula in (a), namely $R = 3 + \frac{1}{181 \cdot 07} I$, was chosen so that the average rate on £546 reckoned from sections (a) and (b) would be the same. However, a more exact calculation leads to

$$R = 3 + \frac{1}{181 \cdot 06} I,$$

instead of the form given.

To find the total amount of tax for an income between £546 and £2,000, we have then only to integrate

$$\frac{23 \cdot 1\dot{6}}{10^3} x - \frac{3 \cdot 2}{10^6} x^2.$$

e.g. for £1,000 we have $\int_0^{1000} \left(\frac{23 \cdot 1\dot{6}}{10^3} x - \frac{3 \cdot 2}{10^6} x^2 \right) dx$ pence, or £43. 17s. 9d.

For £2,000 we have $\int_0^{2000} \left(\frac{23 \cdot 1\dot{6}}{10^3} x - \frac{3 \cdot 2}{10^6} x^2 \right) dx$ pence, or £157. 15s. 7d.

These agree with the figures in the Note to (b).

On the other hand, for an income of £3,000 we must take the part over £2,000 separately, using the formula of (c).

For this part we have

$$\int_{2000}^{3000} \left(-5 + \frac{25 \cdot 1\dot{6}}{10^3} \, x - \frac{3 \cdot 2}{10^6} \, x^2 + \frac{0 \cdot 1\dot{3}}{10^9} \, x^3 \right) dx \text{ pence,}$$

which works out as £165, 18s. 0d.

Thus the amount of tax for £3,000 would be the sum obtained above for £2,000 plus £165. 18s. 0d.; in all, £323. 13s. 7d.

The other sums given in the Note to (c) will be obtained in the same way.

We have dealt so far with the original Act. Two months after it became law, it was followed by an Amending Act, in which it was enacted that

" Where the income of a taxpayer consists of income from personal exertion and income from property the rates of the income tax shall be :

(a) In respect of the income from personal exertion   the rate that would have been applicable if the total taxable income of the taxpayer had been derived exclusively from personal exertion ; and

(b) in respect of the income from property—the rate that would have been applicable if the total taxable income of the ratepayer had been derived from property."

I leave the interpretation of this to the industrious reader. His task would have been an easier one if what the Treasurer called " the beautifully simple terms of the mathematician " had received kinder treatment in the drafting of the original Act.

Sydney, N.S.W., Dec. 9, 1915.

NAPIER'S LOGARITHMS: THE DEVELOP-
MENT OF HIS THEORY.

NAPIER'S LOGARITHMS: THE DEVELOPMENT OF HIS THEORY.

By H. S. CARSLAW, Sc. D.

Introductory.

§ 1. This paper deals with Napier's idea of a logarithm.[1] In my view there are three distinct stages in the development of this idea in his work. In the first he is concerned with a one-one correspondence between the terms of a Geometrical Progression and the terms of an Arithmetical Progression. There are traces of this in the *Constructio*[2] in his use of the series

$$10^7, \ 10^7 \left(1 - \frac{1}{10^7} \right), \ 10^7 \left(1 - \frac{1}{10^7} \right)^2, \text{ etc.,}$$

and in the word logarithm itself, derived from λόγος ἀριθμός, and generally taken to mean " the number of the ratios." In the second he has passed from this correspondence, and his logarithms are given by the well known kinematical definition, which forms the foundation of the theory of the *Constructio*. In the third, referred to in the Appendix to the *Constructio*, he has reached the idea of a logarithm as *defined* by the property :—

[1] In a previous paper in these Proceedings:—The Discovery of Logarithms by Napier of Merchiston—Vol. 48, pp. 42–72, 1914—the question of the construction of the logarithms of the *Canon* has been discussed.

[2] The *Mirifici Logarithmorum Canonis Constructio* was published in 1619, two years after Napier's death, but had been written several years before his *Mirifici Logarithmorum Canonis Descriptio*, published in 1614. I shall refer to these works as the *Constructio* and the *Descriptio*. The *Descriptio* was translated into English by Wright (1616), and Filipowski (1857), the *Constructio* by Macdonald (1889). The former is a rare book, both in the original and in translation. Several of the more important pages are reproduced in the *Napier Tercentenary Memorial Volume*, Plates I – VI, (London, 1915).

The logarithms of proportional numbers have equal differences, with the additional condition that the logarithms of two numbers are given.

In the second and third stages he has obtained what we would now call a function of the independent variable—the number—, but the function of the third stage is more general than that of the second, which it includes as a special case.

If this view is correct, the statement that "Napier's *theory* rests on the establishment of a one-one correspondence between the terms of a geometric series and the terms of an arithmetic series"[1] should not be taken too literally. Further the custom of employing the term "Napier's logarithms" to describe only the logarithms of his *Canon* is unfortunate. It will be seen in the course of this paper that logarithms to the base 10—as we know them—are Napier's logarithms just as much as the logarithms of his *Canon*.

The First Stage.

§ 2. The idea that multiplication and division could be reduced to addition and subtraction by the correlation of a geometrical series and an arithmetical series was not a new one. Aristotle was familiar with it, and since his time many mathematicians had returned to it. If we take the series

$$1, 2, 3, 4, \ 5, \ 6, \ 7, \ 8, \ \ldots\ldots\ 15, \ \ldots\ldots$$
$$2, 4, 8, 16, 32, 64, 128, 256, \ldots\ldots 32768, \ldots\ldots$$

the product of 128 and 256 in the geometrical series can be read off as 32768, which corresponds to 15, the sum of 7 and 8 in the arithmetical series.

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[1] Cajori, Napier's Logarithmic Concept: A Reply. *American Mathematical Monthly*, Vol. 28, p. 71, (1915).

The Swiss Bürgi in his *Arithmetische and Geometrische Progress Tabulen*,[1] constructed some time between 1603 and 1611, but first published in 1620, used the series

$$10 \times 0, 10 \times 1 \quad , \quad 10 \times 2 \quad ,\ldots 10 \times n,\ldots\ldots$$

$$10^8, \quad 10^8\left(1+\frac{1}{10^4}\right), \quad 10^8\left(1+\frac{1}{10^4}\right)^2,\ldots 10^8\left(1+\frac{1}{10^4}\right)^n,\ldots$$

His tables cover the range 10^8 to 10^9, and for all practical purposes are as satisfactory as Napier's Table of Logarithms of 1614. If Napier had simply used the idea of the correspondence between the terms of a geometrical series and the terms of an arithmetical series, his work could not be regarded as so great an advance upon Bürgi's as it really is.

But it is clear that at the beginning of his labours, which extended over a period of twenty years, Napier's mind was working on the same lines as Bürgi's, and that at this stage he used the series

$$0, \quad 1 \quad , \quad 2 \quad , \ldots\ldots$$

$$10^7, \quad 10^7\left(1-\frac{1}{10^7}\right), \quad 10^7\left(1-\frac{1}{10^7}\right)^2, \ldots\ldots$$

in a similar way. This geometrical series occurs in the *Constructio*. He employed it in the calculation of his logarithms, but neither then, nor later, are his logarithms the terms of the corresponding arithmetical series. His word logarithm, (See §1), is evidently a survival of the first stage of his work.

Napier meant his tables to be used in calculations involving the trigonometrical ratios. In his time, the sine, cosine, etc., were lines—or, more exactly, the measures of lines—in a circle of given radius. Napier took the radius

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[1] A facsimile of the title page of Bürgi's work and of one of the pages of the Tables will be found in the *Napier Tercentenary Memorial Volume* (Plates XII and XIII). Comparison with the references in Cantor's *Geschichte der Mathematik*, Tropfke's *Geschichte der Elementar-Mathematik*, and Braunmühl's *Geschichte der Trigonometrie* will show that in none of these works is the title quoted correctly.

as 10^7. It may be that Bürgi chose 10^8 in his tables for a similar reason. With our notation Napier's sines would correspond to 7-Figure Tables of Natural Sines, etc. If greater accuracy were required, the radius was taken as 10^{10}, and sometimes even a higher power of 10 was used. These sines, etc., following Glaisher,[1] we shall refer to as line-sines, etc.

The Second Stage.

§ 3. Napier opened out entirely fresh ground, when he passed to his kinematical definition of the logarithm of a sine or number. By this definition he associated with the sine, as it continually diminished from 10^7 for 90° to zero for 0°, a number which he called its logarithm ; and the logarithm continually increased from 0, for the sine of 90°, to infinity, for the sine of 0°.

The fundamental proposition in Napier's theory in the *Descriptio* (1614) and the *Constructio* (1619) is to be found in Prop. I of the *Descriptio:*

The logarithmes of proportionall numbers and quantities are equally differing.[2]

And in Section 36 of the *Constructio* it appears as *the logarithms of similarly proportioned sines are equidifferent.*

Glaisher has introduced a convenient notation $nl_r\,x$ for Napier's logarithm, in this system, when the radius is 10^r. He also uses $\mathrm{Sin}_r\,x$ for the line-sine of the angle x, when the radius is 10^r, and he keeps the symbol $\sin x$ for the sine in the modern sense of the term. With this notation we have

$$\sin x = \frac{\mathrm{Sin}_r x}{10^r}\ .$$

[1] *Quarterly Journal*, Vol. 46, p. 125 (1916). To this paper I am indebted, not only for a most convenient notation for the different systems of logarithms, but also for an account of Speidell's work, hitherto inaccessible to me.

[2] In quoting the *Descriptio* I follow Wright's version, and for the *Constructio* I adopt Macdonald's.

In this paper I follow his notation, and $\log_e x$ is used in its modern sense for the logarithm of x to the base e, the system commonly called hyperbolic logarithms.

The fundamental theorem, referred to above, can now be stated as follows:—

If $a : b = c : d$, then $nl_r a - nl_r b = nl_r c - nl_r d$.........(1)
Also we are given that　　　　$nl_r \ 10^r = 0.$　..................(2)
Napier's *Canon* consists of a Table of Logarithms in which (1) and (2) are satisfied. His definition of the logarithm by means of the velocities of two points moving in two different lines leads to the formula

$$nl_r x = 10^r \log_e \left(\frac{10^r}{x} \right).$$

But, of course, neither this, nor the fact that his function $nl_r x$ has -1 for its differential coefficient, when $x = 10^r$, could be known in his time.

The Third Stage.

§ 4. Since $u \, v : u = v : 1,$
　　we have $nl_r \, (uv) - nl_r u = nl_r v - nl_r 1.$

Thus $nl_r(uv) = nl_r u + nl_r v - nl_r 1,$
and it must be remembered that $nl_r 1$ is not zero.

When $r = 7$, $nl_r 1 = 161180896{\cdot}38$ (Cf. *Constructio*, Section 53).[1]

Similarly $nl_r \, (u/v) = nl_r u - nl_r v + nl_r 1.$

Thus multiplication and division are changed into addition and subtraction. But the logarithms of numbers with the same figures in the same order cannot be read off from one another, since, in this system,

$$nl_r \, (10^m a) = nl_r a - m \, (nl_r 1 - nl_r 10),$$

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[1] The error in Napier's Second Table affects the accuracy of his Canon and this number should be 161180956·51. The alteration can be made from the corrected result given by Macdonald in his English translation of the *Constructio* pp. 94-5, for it is not difficult to show that $nl_r 1 = 7 \, nl_r 10^r$.

and $nl_7 1 - nl_7 10 = 23025842\cdot 31$ (Cf. *Constructio*, Section 53).[1]

It is obvious that if a system of logarithms could be devised in which the logarithm of unity is zero and the logarithm of 10 is unity, the calculations would be immensely simplified, and the table curtailed; because one of the chief defects of Napier's *Canon*, as well as of Bürgi's Tables, was that, if the numbers did not come within the range covered by it, more or less awkward calculations were needed to overcome this difficulty.

Napier's *Canon* was first printed in the *Descriptio* (1614). After his death in 1617 the *Constructio* was published by the care of his son. It had been written several years before the *Descriptio*. To this work was added an Appendix, by the hand of Napier himself, "On the Construction of another and *better kind of* Logarithms, *namely* one in which the Logarithm of unity is 0." This Appendix begins with the words:—

"*Among the various improvements of Logarithms, the more important is that which adopts a cypher as the Logarithm of unity, and 10,000,000,000 as the Logarithm of either one-tenth of unity or ten times unity. Then, these being once fixed, the Logarithms of all other numbers necessarily follow.*"

It is clear from Napier's words that, when he wrote the Appendix, not only did he see the advantage of such a system, but he was in a position to draw up a Table of Logarithms in which these conditions would be satisfied. Indeed he gives three distinct methods of finding these logarithms. The kinematical definition of the logarithm was superseded, and the correspondence between the terms

[1] This number should be $23025850\cdot 93$, since it is easy to show that $nl_1 1 - nl_7 10 = nl_7 10^9$, and Macdonald gives the corrected logarithm of 10^9 (*loc. cit.*, pp. 94-5).

of a geometrical series and the terms of an arithmetical
series was left far behind.   This is the third and final stage
of his work.

Briggs and Napier.

§ 5. In the change from the logarithms of the Canon to
this "better kind of logarithms" Briggs was associated
with Napier; but, chiefly because of the unsatisfactory
account of the matter given by Hutton in his *History of
Logarithms*,[1] the share of the former in the discovery has
been exaggerated.   The fault is not due to Briggs; and,
though his reference to the question in the preface to the
Arithmetica Logarithmica (1624) is familiar, I reproduce
it again here:—

"I myself, when expounding publicly in London their doctrine
to my auditors in Gresham College, remarked that it would be
much more convenient that 0 should stand for the logarithm of
the whole sine, as in the Canon Mirificus, but that the logarithm
of the tenth part of the whole sine, that is to say, 5 degrees 44
minutes 21 seconds, should be 10,000,000,000.   Concerning that
matter I wrote immediately to the author himself; and as soon as
the season of the year and the vacation time of my public duties
of instruction permitted, I took journey to Edinburgh, where,
being most hospitably received by him, I lingered for a whole
month.   But as we held discourse concerning this change in the
system of logarithms, he said that for a long time he had been
sensible of the same thing, and had been anxious to accomplish
it, but that he had published those he had already prepared, until
he could construct tables more convenient, if other weighty
matters and his frail health would permit him to do.   But he
conceived that the change ought to be affected in this manner,
that 0 should become the logarithm of unity, and 10,000,000,000
that of the whole sine; which I could not but admit was by far the
most convenient of all.   So, rejecting those which I had already

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[1] Hutton's *Tracts on Mathematical and Philosophical Subjects*, Vol. I,
Tract 20.

prepared, I commenced, under his encouraging counsel, to ponder seriously about the calculation of these tables."

Napier also mentions his discovery of the new system in the dedication of his *Rabdologia* (1617) in a passage quoted in my previous paper.[1]

It will be seen from Briggs' own words, that the modification which he suggested to Napier was to keep the logarithm of the radius as zero, but to take the logarithm of one-tenth of the radius as 10,000,000,000.   His reference to the *Canon* is sufficient to show that he does not look upon the radius as unity.   In the construction of the Table of Logarithms, after Napier's death, he takes it as 10^{10}, and it is for this reason that the characteristics 9, 8, etc., are to be found in the logarithms of the sines, etc.

Using the notation $bl_r x$ for the logarithm of x in the system suggested by Briggs when the radius is 10^r, we have
$$bl_r a - bl_r b = bl_r c - bl_r d,$$
when $a : b = c : d$.

Also $bl_r 10^r = 0$, and $bl_r 10^{r-1} = 10^{10}$.

In this system we have
$$bl_r (uv) = bl_r u + bl_r v - bl_r 1,$$
$$bl_r (u/v) = bl_r u - bl_r v + bl_r 1.$$
$$\text{Also } bl_{10} 10^{10} = 10\ bl_{10} 10 - 9\ bl_{10} 1 = 0$$
$$bl_{10} 10^9 = 9\ bl_{10} 10 - 8\ bl_{10} 1 = 10^{10}.$$

Thus $bl_{10} 10 = 9 \times 10^{10}$ and $bl_{10} 1 = 10 \times 10^{10}$.

The advantage of the new system consists in the fact that the logarithms of numbers with the same figures in the same order could be read off from each other, since we have $bl_r (10^m a) = bl_r a - m \times 10^{10}$.

§ 6. The change upon which Napier had resolved, previous to Briggs' visit, was a much more important one.   He "conceived that the change ought to be affected in this

manner, that 0 should become the logarithm of unity, and 10,000,000,000 that of the whole sine." And finally in the Appendix we see that he often passes from logarithms of sines, and now drops all reference to the radius.

In the new system, logarithms were to be *defined* by the relations:—

If $a : b = c : d$, then $nl\ a - nl\ b = nl\ c - nl\ d$,

with $nl\ 1 = 0$ and $nl\ 10 = 10^{10}$.

It need hardly be added that 10^{10} was taken for the logarithm of 10 instead of unity, for the same reason that 10^7 (or 10^{10}) was taken for the radius in dealing with the trigonometrical ratios.

Later Briggs takes the logarithm of 10 as unity, and introduces the notation of decimal fractions in his Tables, a notation employed, probably for the first time, by Napier himself.

If this account of the growth of the idea of a logarithm in Napier's work is correct,[1] it seems unfortunate that the term Napier's logarithms is usually confined to the logarithms of his *Canon*. His "better kind of logarithms" actually consists of the logarithms now in daily use—the logarithms which we call logarithms to the base 10. In some textbooks they receive the awkward name Briggsian logarithms. Certainly Briggs calculated them, and the rapidity and industry with which he performed this immense work in computation will always be the admiration of mathematicians. But the discovery of the system was Napier's, and the logarithms are as much Napier's logarithms as those of his *Canon*.

Speidell's New Logarithmes (1619).

§ 7. In most accounts of the discovery of logarithms reference is made to Speidell's *New Logarithmes* (London,

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[1] See also Gibson's paper in the *Napier Tercentenary Memorial Volume,* pp. 111 – 137.

1619), and it is stated that they contain the first table of logarithms to the base e.[1]   Attention is also usually called to the fact that, while logarithms to the base e are frequently spoken of as Napierean logarithms, they are quite different from the logarithms of Napier's *Canon;* and it is pointed out that the place of the number e in the theory of logarithms and the possibility of defining logarithms as exponents were discoveries of a much later day.   These two statements, at first sight, seem inconsistent.   A word or two regarding Speidell's system will make the matter clearer, and will also confirm the view I have taken above as to Napier's final conception of the logarithm.

Speidell's *New Logarithmes*, like Napier's *Canon*, refer to the trigonometrical ratios.   Using Glaisher's notation $sl_r x$ for Speidell's logarithm of x when the radius is 10^r, we have $$sl_r x = 10^{r+1} - nl_r x.$$

It follows that
$$sl_r (uv) = sl_r u + sl_r v - sl_r 1,$$
$$sl (uv) = sl_r u - sl_r v + sl_r 1,$$
and $sl_r 1$ is not zero.

The sole advantages of this system was that it avoided the use of negative quantities in calculation with logarithms.   Such quantities were then outside the range of the "vulgar and common arithmetic."

Since $nl_r x = 10^r \log_e \left(\dfrac{10^r}{x} \right),$

we have $sl_r x = 10^{r+1} + 10^r \log_e \left(\dfrac{x}{10^r} \right).$

Thus $sl_r \, Sin_r x = 10^{r+1} + 10^r \log_e \left(\dfrac{Sin_r x}{10^r} \right)$
$$= 10^r (10 + \log_e \sin x).$$

[1] In Glaisher's paper already referred to, he published the interesting discovery that an Appendix (1618) to Wright's English translation of the *Descriptio* contains a table of hyperbolic logarithms by an anonymous author, whom he identifies with Oughtred.

In a sense Speidell's *New Logarithmes* may be said to be hyperbolic logarithms, but the sense is the same as that in which the logarithms of Napier's *Canon* are sometimes said to be logarithms to the base e^{-1}. However this is a misuse of the term.' Still Speidell's logarithms of sines, from the accident that the sine is now used in a different sense, have actually the same figures as our hyperbolic logarithms of sines.

In the *New Logarithmes* (1619) he takes the radius as 10^5, so that these tables give

$$sl_b \operatorname{Sin}_b x = 10^5 (10 + \log_e \sin x).$$

§ 8. But subsequently Speidell *did* publish a table of hyperbolic logarithms of numbers, which gives the values of $10^6 \log_e x$ for numbers 1 to 1,000. This table probably appeared either separately, or attached to an impression of the *New Logarithmes*, in 1622 or 1623. In this system he takes

$$sl_r x = nl_r 1 - nl_r x.$$

It follows that

$$sl_r (uv) = sl_r u + sl_r v,$$
$$sl_r (u/v) = sl_r u - sl_r v;$$

and since

$$nl_r x = 10^r \log_e \left(\frac{10^r}{x}\right),$$

we have

$$sl_r x = 10^r \log_e x.$$

But it is clear that in both Speidell's systems of logarithms the connection with hyperbolic logarithms is accidental, and the same is true of the logarithms discovered by Glaisher, to which reference is made at the beginning of this section.

Like Napier and Briggs, Speidell sees that the fundamental property, that the logarithms of proportional numbers have equal differences, can be taken as the starting

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' *Cf.* Glaisher, *loc. cit.*, p. 146, footnote.

point of the theory; and that, if the logarithm of unity is zero, the logarithms of the product and the quotient of two numbers are, respectively, the sum and difference of their separate logarithms.

§ 9. The Differential Equation satisfied by the logarithm of x.

We have seen that the theory of the different systems of logarithms described in the previous pages rests upon the fundamental property:—

If $a : b = c : d$, then $\lambda(a) - \lambda(b) = \lambda(c) - \lambda(d)$, where $\lambda(x)$ stands for the logarithm of x.

The function $\lambda(x)$, therefore, satisfies the equation

$$\lambda(x + h) - \lambda(x) = \lambda\left(1 + \frac{h}{x}\right) - \lambda(1).$$

$$\therefore \quad \frac{\lambda(x+h) - \lambda(x)}{h} = \frac{1}{x} \left\{ \frac{\lambda\left(1 + \frac{h}{x}\right) - \lambda(1)}{\frac{h}{x}} \right\}$$

Proceeding to the limit $h \to 0$, of course keeping x fixed, we have $\qquad \lambda'(x) = \dfrac{A}{x}$, where $A = \lambda'(1)$.

Therefore $\lambda(x) = A \log_e x + B$,

and the system is made definite by adding two other conditions.

In Napier's *Canon*, writing ρ for the radius, we have
$$nl\, x = A \log_e x + B,$$
with $\qquad nl\, \rho = 0$, and $nl'\, \rho = -1$.

Therefore $nl\, x = \rho \log_e\left(\dfrac{\rho}{x}\right)$.

In Briggs' modification of the system, we have
$$bl\, x = A \log_e x + B,$$
with $\qquad bl\, \rho = 0$ and $bl\left(\dfrac{\rho}{10}\right) = 10^{10}$.

Thus $bl\, x = 10^{10} \dfrac{\log_e\left(\dfrac{\rho}{x}\right)}{\log_e 10} = 10^{10} \log_{10}\left(\dfrac{\rho}{x}\right)$.

And Napier's final form is, of course,

$$nl\ x\ =\ 10^{10}\ \log_{10}\ x.$$

Bürgi's *Arithmetische und Geometrische Progress Tabulen* also come under the same law. If the terms in the Arithmetical Progression are taken as the logarithms of the terms in the Geometrical Progression, and $Bl\ x$ stands for what I may call Bürgi's logarithm of x, we have

$$Bl\ x\ =\ 10\ \frac{\log_e\left(\frac{x}{10^8}\right)}{\log_e\left(1+\frac{1}{10^4}\right)}\ =\ 10\ \log_{1+\frac{1}{10^4}}\left(\frac{x}{10^8}\right)$$

for $x\ =\ 10^8\left(1+\frac{1}{10^4}\right)^s$, s being any positive integer.

Finally, treating Napier's series

$$0,\ \ \ 1,\ \ \ \ \ \ \ \ 2\ldots\ldots$$
$$10^7,\ 10^7\left(1-\frac{1}{10^7}\right),\ 10^7\left(1-\frac{1}{10^7}\right)^2,\ldots\ldots$$

in the same way, and denoting this logarithm by $Nl\ x$, we have

$$Nl\ x\ =\ \frac{\log_e\left(\frac{x}{10^7}\right)}{\log_e\left(1-\frac{1}{10^7}\right)}\ =\ \log_{1-\frac{1}{10^7}}\left(\frac{x}{10^7}\right),$$

for $x\ =\ 10^7\left(1-\frac{1}{10^7}\right)^s$, s being any positive integer.

A Trigonometrical Sum and the Gibbs' Phenomenon in Fourier's Series.[*]

By H. S. CARSLAW.

§ 1. If $f(x)$ is a function which can be expanded in a Fourier's Series in the interval $0 \leqq x \leqq 2\pi$, with a discontinuity at $x = a$ such that $f(a-0)$ and $f(a+0)$ exist, the sum of the Fourier's Series for $x = a$ is $\frac{1}{2}\{f(a+0)+f(a-0)\}$.

Denoting by $S_n(x)$ the sum of the terms up to and including those in sin nx and cos nx, the curves $y = S_n(x)$ are usually spoken of as the approximation curves for the series. Up till 1899 it was believed that each approximation curve, for large values of n, passes at a steep gradient from a point near $(a, f(a-0))$ to a point near $(a, \frac{1}{2}(f(a+0)+f(a-0)))$, and then on to a point near $(a, f(a+0))$, afterwards oscillating about the curve $y = f(x)$ till another discontinuity of $f(x)$ is met.

In 1899 J. Willard Gibbs pointed out[†] that the approximation curves for the sine series

$$2(\sin x - \tfrac{1}{2}\sin 2x + \tfrac{1}{3}\sin 3x - \dots)$$

do not behave in this way.

In the interval $0 \leqq x \leqq 2\pi$, the sum of this series is $f(x)$, where $f(x)$ is defined as follows:

$$f(0) = f(2\pi) = 0,$$
$$f(x) = x, \ 0 < x < \pi,$$
$$f(x) = x - 2\pi, \ \pi < x < 2\pi.$$

Gibbs stated in effect that the curve $y = S_n(x)$ for this series, for large values of n, rises just before $x = \pi$ to a point very nearly at a height $2\int_0^\pi \frac{\sin x}{x}dx$ above the axis of x, passes from that point through $(\pi, 0)$ at a steep gradient to a point very nearly at the same distance $2\int_0^\pi \frac{\sin x}{x}dx$ below the axis, while in the rest of the interval $0 \leqq x \leqq 2\pi$ it oscillates above and below the curve $y = f(x)$.

His statement was not accompanied by any proof. Though the remainder of the correspondence, of which his letter formed a part, attracted no little attention, this remarkable observation remained practically unnoticed for several years. In 1906 Bôcher returned to the subject in a memoir on Fourier's Series,[*] and extended Gibbs' results in two directions.

First of all he discussed the series

$$\sin x + \tfrac{1}{2}\sin 2x + \tfrac{1}{3}\sin 3x + \dots,$$

which, in the interval $0 \leq x \leq 2\pi$, represents the function $f(x)$ defined as follows:

$$\left. \begin{array}{l} f(0) = f(2\pi) = 0, \\ f(x) = \tfrac{1}{2}(\pi - x) \dots 0 < x < 2\pi. \end{array} \right\}$$

He showed that the approximation curve

$$y = \sin x + \frac{1}{2}\sin 2x + \dots + \frac{1}{n}\sin nx = S_n(x),$$

in the interval $0 \leq x \leq 2\pi$, and for large values of n, takes the form of a wavy curve which keeps crossing and recrossing the line $y = \tfrac{1}{2}(\pi - x)$ and reaches its greatest distance from that line (distances being measured parallel to the axis of y) at the points $x_1, x_2, \dots, x_{2n}$, where $x_r = \dfrac{2r\pi}{2n+1}$.

Further, these greatest distances in the r-th wave are, for large values of n, approximately equal to their limiting values

$$\tfrac{1}{2}\pi - \int_0^{r\pi} \frac{\sin x}{x}\, dx.$$

In the second place he showed that the phenomenon in question also appears in the Fourier's Series for a large class of functions. How large this class is will appear in the concluding section of this paper.

In Bôcher's own words:[†] If $S_n(x)$ denotes the sum of the Fourier's expansion of $f(x)$, the curve $y = S_n(x)$ will, for large values of n, pass in almost a vertical direction through a point whose abscissa is a and whose ordinate is almost $\tfrac{1}{2}\{f(a+0) + f(a-0)\}$. The curve then rises and falls abruptly on the two sides of this point to the neighborhood of the curve

* *Annals of Mathematics* (2), Vol. VII (1906). See also a recent paper in *Crelle's Journal*, Bd. 144 (1914), entitled "On Gibbs' Phenomenon."

Reference should also be made to Runge's "Theorie und Praxis der Reihen" (1904), pp. 170–180. A certain series is there discussed, and the nature of the jump in the approximation curve described. But no reference is made to Gibbs, and the example seems to have been regarded as quite an isolated one.

† *Loc. cit., Annals of Mathematics*, p. 131. Both Theorems I and II, p. 131, should be noted.

$y=f(x)$, and oscillates about this curve, lying alternately above and below it. The highest (or lowest) point of the k-th wave to the right and left of a will, for large values of n, be approximately at the points

$$a \pm \frac{2k\pi}{2n+1},$$

and the height of these waves will be approximately

$$\frac{f(a+0)-f(a-0)}{\pi} P_k,$$

$$\left(\text{where } P_k = \tfrac{1}{2}\pi - \int_0^{k\pi} \frac{\sin x}{x} dx\right).$$

In the above sentence, a is a value of x at which $f(x)$ has an ordinary discontinuity, and Bôcher adds a footnote to the effect that "it must be borne in mind that we measure the height of a wave from the curve $y=f(x)$ in a direction parallel to the axis of y."

§ 2.   In the function studied by Bôcher, $\tfrac{1}{2}(\pi-x)$,

$$S_n(x) = \sin x + \frac{1}{2}\sin 2x + \dots + \frac{1}{n}\sin nx$$

$$= \int_0^x (\cos \alpha + \cos 2\alpha + \dots + \cos n\alpha)\, d\alpha$$

$$= \tfrac{1}{2}\int_0^x \frac{\sin(n+\tfrac{1}{2})\alpha}{\sin \tfrac{1}{2}\alpha}\, d\alpha - \tfrac{1}{2}x.$$

The properties of the maxima and minima of $S_n(x)$ are not so easy to obtain, nor are they so useful in this case as those of

$$R_n(x) = \tfrac{1}{2}(\pi-x) - S_n(x)$$

$$= \tfrac{1}{2}\pi - \tfrac{1}{2}\int_0^x \frac{\sin(n+\tfrac{1}{2})\alpha}{\sin \tfrac{1}{2}\alpha}\, d\alpha.$$

It is the maxima and minima of $R_n(x)$ with which Bôcher deals in his memoir.

Gronwall has discussed [*] the somewhat complicated properties of the maxima and minima of $S_n(x)$ for this series, and deduced Gibbs' Phenomenon for the first wave, and the general case of Fourier's Series.

In this paper I use the series

$$2(\sin x + \tfrac{1}{3}\sin 3x + \tfrac{1}{5}\sin 5x + \dots),$$

[*] *Mathematische Annalen*, Bd. LXXII (1912). Some of Gronwall's results had been published a few months earlier by Dunham Jackson in a paper in the *Rendiconti di Circolo Matematico di Palermo*, T. XXXII (1911).

which, in the interval $-\pi \leqq x \leqq \pi$,* represents the function $f(x)$ defined by the equations

$$f(-\pi) = f(0) = f(\pi) = 0,$$
$$f(x) = -\tfrac{1}{2}\pi \ldots -\pi < x < 0,$$
$$f(x) = \tfrac{1}{2}\pi \ldots 0 < x < \pi.$$

I take $S_n(x)$ for the sum of the first n terms of this series, so that

$$S_n(x) = 2\left(\sin x + \tfrac{1}{3}\sin 3x + \ldots + \frac{1}{2n-1}\sin(2n-1)x\right).$$

A number of interesting properties of the turning points of $y = S_n(x)$ are obtained by quite simple methods; and all the features of Gibbs' Phenomenon for this series follow immediately from these properties.

In the concluding article the extension to the general case of Fourier's Series is given; but the method does not differ materially from that of Bôcher.

It is, of course, not an unusual thing that the curves $y = S_n(x)$ for a series, whose terms are continuous functions, differ considerably, even for large values of n, from the curve $y = \underset{n \to \infty}{\mathrm{Lt.}}(S_n(x)) = S(x)$.

They certainly do so in the neighborhood of a point where $S(x)$, the sum of the series, is discontinuous. And they also may do so in the neighborhood of a point where $S(x)$ is continuous.†

Ex. (i). If
$$S_n(x) = \frac{nx}{1+n^2x^2}, \quad x \geqq 0,$$
we have
$$S(x) = 0, \qquad x \geqq 0.$$

In this case $S_n(x)$ has a maximum value $\frac{1}{2}$ at $x = \frac{1}{n}$. As n gets larger and larger, this summit is pushed towards $x = 0$ but its height remains equal to $\frac{1}{2}$.

Ex. (ii). If
$$S_n(x) = \frac{n^2x}{1+n^3x^3}, \quad x \geqq 0,$$
we have
$$S(x) = 0, \qquad x \geqq 0.$$

In this case $S_n(x)$ has a maximum value $\frac{1}{2}n^{\frac{1}{3}}$ at $x = \frac{1}{n^{\frac{1}{3}}}$. As n gets larger and larger, this summit is pushed towards $x = 0$ but its height increases without limit.

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* It is more convenient for my purpose to take the interval $-\pi \leqq x \leqq \pi$ than $0 \leqq x \leqq 2\pi$. This does not affect the argument to any extent.

† Cf. Osgood, *Bulletin of the American Math. Soc.* (2), Vol. III (1897), p. 63; AMERICAN JOURNAL OF MATHEMATICS, Vol. XIX (1897), p. 155; Hobson, "Theory of Functions of a Real Variable," p. 480; Bromwich, "Theory of Infinite Series," p. 110; Carslaw, "Fourier's Series and Integrals," Ch. III.

. The existence of maxima (or minima) of $S_n(x)$, the abscissæ of which tend towards a (a being a value of x for which the sum of the series is discontinuous), while their ordinates remain at a finite distance from $S(a+0)$ and $S(a-0)$, as n increases, is the chief feature of the Gibbs' Phenomenon in Fourier's Series. And it is most remarkable that its occurrence in Fourier's Series remained undiscovered till so recent a date.[*]

<div style="text-align:center">THE TRIGONOMETRICAL SUM</div>

$$S_n(x) = 2\left(\sin x + \tfrac{1}{3}\sin 3x + \ldots + \frac{1}{2n-1}\sin(2n-1)x\right).$$

§ 3. If we define $f(x)$ by the equations

$$\left.\begin{array}{l} f(-\pi) = f(0) = f(\pi), \\ f(x) = \tfrac{1}{2}\pi \ldots 0 < x < \pi, \\ f(x) = -\tfrac{1}{2}\pi \ldots -\pi < x < 0, \end{array}\right\}$$

the Fourier's Series for $f(x)$ in the interval $-\pi \leq x \leq \pi$ is

$$2(\sin x + \tfrac{1}{3}\sin 3x + \tfrac{1}{5}\sin 5x + \ldots).$$

We denote by $S_n(x)$ this sum up to and including the term in $\sin(2n-1)x$. Then

$$S_n(x) = 2\int_0^x (\cos x + \cos 3x + \ldots + \cos(2n-1)x)\,dx = \int_0^x \frac{\sin 2n\alpha}{\sin \alpha}\,d\alpha.$$

Since $S_n(x)$ is an *odd* function, we need only consider the interval $0 \leq x \leq \pi$.

We proceed to obtain the properties of the maxima and minima of this function $S_n(x)$.

I. Since, for any integer m, $\sin(2m-1)(\tfrac{1}{2}\pi+x') = \sin(2m-1)(\tfrac{1}{2}\pi-x')$, it follows from the series that $S_n(x)$ *is symmetrical about* $x = \tfrac{1}{2}\pi$, *and when* $x=0$ *and* $x=\pi$ *it is zero.*

II. *When* $0 < x < \pi$, $S_n(x)$ *is positive.*

From (I) we need only consider $0 < x \leq \tfrac{1}{2}\pi$. We have

$$S_n(x) = \int_0^x \frac{\sin 2n\alpha}{\sin \alpha}\,d\alpha = \frac{1}{2n}\int_0^{2nx} \frac{\sin \alpha}{\sin \dfrac{\alpha}{2n}}\,d\alpha, \ 0 < x \leq \tfrac{1}{2}\pi.$$

The denominator in the integrand is positive and continually increases in the

* Cf. also Weyl: (i) "Die Gibbs'sche Erscheinung in der Theorie der Kugel-Funktionen," *Rend. Circ. Mat. d. Palermo,* T. XXIX (1910); (ii) "Über die Gibbs'sche Erscheinung und verwandte Konvergenzphänomene," *ibid.,* T. XXX (1910).

interval of integration. By considering the successive waves in the graph of $\sin\alpha\operatorname{cosec}\dfrac{\alpha}{2n}$, the last of which may or may not be completed, it is clear that the integral is positive.

III.　*The turning points of $y = S_n(x)$ are given by*

$$\begin{cases} x_1 = \dfrac{\pi}{2n},\ x_3 = \dfrac{3\pi}{2n},\ \ldots,\ x_{2n-1} = \dfrac{2n-1}{2n}\pi\ \ (maxima), \\[2mm] x_2 = \dfrac{\pi}{n},\ x_4 = \dfrac{2\pi}{n},\ \ldots,\ x_{2(n-1)} = \dfrac{n-1}{n}\pi\ \ (minima). \end{cases}$$

We have

$$y = \int_0^x \frac{\sin 2n\alpha}{\sin\alpha}\,d\alpha,\ \text{and}\ \frac{dy}{dx} = \frac{\sin 2nx}{\sin x}.$$

The result follows at once.

IV.　*As we proceed from $x = 0$ to $x = \tfrac{1}{2}\pi$, the heights of the maxima continually diminish, and the heights of the minima continually increase, n being kept fixed.*

Consider two consecutive maxima in the interval $0 < x \leqq \tfrac{1}{2}\pi$, namely, $S_n\!\left(\dfrac{2m-1}{2n}\pi\right)$ and $S_n\!\left(\dfrac{2m+1}{2n}\pi\right)$, m being a positive integer less than or equal to $\tfrac{1}{2}(n-1)$. We have

$$S_n\!\left(\frac{2m-1}{2n}\pi\right) - S_n\!\left(\frac{2m+1}{2n}\pi\right) = \frac{1}{2n}\int_{(2m+1)\pi}^{(2m-1)\pi}\frac{\sin\alpha}{\sin\dfrac{\alpha}{2n}}\,d\alpha$$

$$= -\frac{1}{2n}\left\{\int_{(2m-1)\pi}^{2m\pi}\frac{\sin\alpha}{\sin\dfrac{\alpha}{2n}}\,d\alpha + \int_{2m\pi}^{(2m+1)\pi}\frac{\sin\alpha}{\sin\dfrac{\alpha}{2n}}\,d\alpha\right\}.$$

The denominator in both integrands is positive and it continually increases in the interval $(2m-1)\pi \leqq \alpha \leqq (2m+1)\pi$; also the numerator in the first is continually negative and in the second continually positive; the absolute values for elements at equal distances from $(2m-1)\pi$ and $2m\pi$ being the same.

Thus the result follows. Similarly for the minima, we have to examine the sign of

$$S_n\!\left(\frac{m-1}{n}\pi\right) - S_n\!\left(\frac{m}{n}\pi\right),$$

where m is a positive integer less than or equal to $\tfrac{1}{2}n$.

V. *The first maximum to the right of* $x=0$ *is at* $x=\dfrac{\pi}{2n}$ *and its height continually diminishes as n increases. When n tends to infinity, its limit is*

$$\int_0^\pi \frac{\sin x}{x}\,dx.$$

We have

$$S_n\left(\frac{\pi}{2n}\right) = \int_0^{\frac{\pi}{2n}} \frac{\sin 2n\alpha}{\sin \alpha}\,d\alpha = \frac{1}{2n}\int_0^\pi \sin\alpha\,\operatorname{cosec}\frac{\alpha}{2n}\,d\alpha,$$

and

$$S_n\left(\frac{\pi}{2n}\right) - S_{n+1}\left(\frac{\pi}{2n+2}\right) = \int_0^\pi \sin\alpha\left(\frac{1}{2n}\operatorname{cosec}\frac{\alpha}{2n} - \frac{1}{2n+2}\operatorname{cosec}\frac{\alpha}{2n+2}\right)d\alpha.$$

Since $\alpha/\sin\alpha$ continually increases from 1 to ∞, as α passes from 0 to π, it is clear that in the interval with which we have to deal

$$\frac{1}{2n}\operatorname{cosec}\frac{\alpha}{2n} - \frac{1}{2n+2}\operatorname{cosec}\frac{\alpha}{2n+2} > 0.$$

Thus

$$S_n\left(\frac{\pi}{2n}\right) - S_{n+1}\left(\frac{\pi}{2(n+1)}\right) > 0.$$

But, from (I), $S_n(x)$ is positive when $0 < x < \pi$.

It follows that $S_n\left(\dfrac{\pi}{2n}\right)$ tends to a limit as n tends to infinity.

The value of this limit can be obtained by the method used by Bôcher for the integral $\displaystyle\int_0^\pi \frac{\sin(n+\frac12)\alpha}{\sin\frac12\alpha}\,d\alpha.$[*] But it is readily obtained from the definition of the Definite Integral as the limit of a sum.

For we have

$$S_n\left(\frac{\pi}{2n}\right) = 2\left(\frac{\pi}{2n}\right)\left\{\frac{2n}{\pi}\sin\frac{\pi}{2n} + \frac{2n}{3\pi}\sin\frac{3\pi}{2n} + \ldots + \frac{2n}{(2n-1)\pi}\sin\frac{2n-1}{2n}\pi\right\}$$

$$= 2\sum_{\substack{m=1\\2nh=\pi}}^{2n}\left(\frac{\sin mh}{mh}h\right) - \sum_{\substack{m=1\\nh=\pi}}^{n}\left(\frac{\sin mh}{mh}h\right).$$

Therefore

$$\operatorname*{Lt.}_{n\to\infty} S_n\left(\frac{\pi}{2n}\right) = 2\int_0^\pi \frac{\sin x}{x}\,dx - \int_0^\pi \frac{\sin x}{x}\,dx = \int_0^\pi \frac{\sin x}{x}\,dx.$$

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[*] *Loc. cit., Annals of Mathematics*, p. 124. Also Hobson, *loc. cit.*, p. 649.

VI.   The result obtained in (V) for the first wave is a special case of the following:

The r-th maximum to the right of $x=0$ is at $x_{2r-1} = \dfrac{2r-1}{2n}\pi$, and its height continually diminishes as n increases, r being kept constant. When n tends to infinity, its limit is $\displaystyle\int_0^{(2r-1)\pi} \dfrac{\sin x}{x}\,dx$, which is greater than $\tfrac{1}{2}\pi$.

The r-th minimum to the right of $x=0$ is at $x_{2r} = \dfrac{r}{n}\pi$, and its height continually increases as n increases, r being kept constant. When n tends to infinity, its limit is $\displaystyle\int_0^{2r\pi} \dfrac{\sin x}{x}\,dx$, which is less than $\tfrac{1}{2}\pi$.

To prove these theorems we consider first the integral

$$\int_0^{m\pi} \sin \alpha \left(\frac{1}{2n} \operatorname{cosec} \frac{\alpha}{2n} - \frac{1}{2n+2} \operatorname{cosec} \frac{\alpha}{2n+2} \right) d\alpha,$$

m being a positive integer less than or equal to $2n-1$, so that $0 < \dfrac{\alpha}{2n} < \pi$ in the interval of integration.

Then

$$F(\alpha) = \frac{1}{2n} \operatorname{cosec} \frac{\alpha}{2n} - \frac{1}{2n+2} \operatorname{cosec} \frac{\alpha}{2n+2} > 0$$

in this interval.   (Cf. (V)).

Further,

$$F'(\alpha) = \frac{1}{(2n+2)^2} \cos \frac{\alpha}{2n+2} \operatorname{cosec}^2 \frac{\alpha}{2n+2} - \frac{1}{(2n)^2} \cos \frac{\alpha}{2n} \operatorname{cosec}^2 \frac{\alpha}{2n}$$

$$= \alpha^{-2} \left\{ \phi^2 \cos \phi \operatorname{cosec}^2 \phi - \psi^2 \cos \psi \operatorname{cosec}^2 \psi \right\},$$

where $\phi = \alpha/(2n+2)$ and $\psi = \alpha/2n$.

But

$$\frac{d}{d\phi} (\phi^2 \cos \phi \operatorname{cosec}^2 \phi) = -\phi \operatorname{cosec}^3 \phi \left[\phi (1 \mp \cos \phi)^2 \pm 2 \cos \phi (\phi \mp \sin \phi) \right].$$

And the right-hand side of the equation will be seen to be negative, choosing the upper signs for $0 < \phi < \tfrac{1}{2}\pi$ and the lower for $\tfrac{1}{2}\pi < \phi < \pi$.

Therefore $\phi^2 \cos \phi \operatorname{cosec}^2 \phi$ diminishes as ϕ increases from 0 to π.

It follows, from the expression for $F'(\alpha)$, that $F'(\alpha) > 0$, and $F(\alpha)$ increases with α in the interval of integration.

The curve

$$y = \sin x \left(\frac{1}{2n} \operatorname{cosec} \frac{x}{2n} - \frac{1}{2n+2} \operatorname{cosec} \frac{x}{2n+2} \right), \ldots, 0 < x < m\pi,$$

thus consists of a succession of waves of length π, alternately above and below the axis, and the absolute values of the ordinates at points at the same distance from the beginning of each wave continually increase.

It follows that, when m is equal to $2, 4, \ldots, 2(n-1)$, the integral

$$\int_0^{m\pi} \sin \alpha \left(\frac{1}{2n} \operatorname{cosec} \frac{\alpha}{2n} - \frac{1}{2n+2} \operatorname{cosec} \frac{\alpha}{2n+2} \right) d\alpha$$

is negative; and, when m is equal to $1, 3, \ldots, 2n-1$, this integral is positive.

Returning to the maxima and minima, we have, for the r-th maximum to the right of $x=0$,

$$S_n(x_{2r-1}) - S_{n+1}(x_{2r-1}) = \int_0^{\frac{2r-1}{2n}\pi} \frac{\sin 2n\alpha}{\sin \alpha} d\alpha - \int_0^{\frac{2r-1}{2(n+1)}\pi} \frac{\sin 2(n+1)\alpha}{\sin \alpha} d\alpha$$

$$= \int_0^{(2r-1)\pi} \sin \alpha \left(\frac{1}{2n} \operatorname{cosec} \frac{\alpha}{2n} - \frac{1}{2n+2} \operatorname{cosec} \frac{\alpha}{2n+2} \right) d\alpha.$$

Therefore from the above argument, $S_n(x_{2r-1}) > S_{n+1}(x_{2r-1})$.

Also for the r-th minimum to the right of $x=0$, we have

$$S_n(x_{2r}) - S_{n+1}(x_{2r}) = \int_0^{2r\pi} \sin \alpha \left(\frac{1}{2n} \operatorname{cosec} \frac{\alpha}{2n} - \frac{1}{2n+2} \operatorname{cosec} \frac{\alpha}{2n+2} \right) d\alpha,$$

and $S_n(x_{2r}) < S_{n+1}(x_{2r})$.

By an argument similar to that at the close of (V) we have

$$\operatorname*{Lt.}_{n \to \infty} S_n(x_r) = \int_0^{r\pi} \frac{\sin x}{x} dx.^*$$

It is clear that these limiting values are all greater than $\frac{1}{2}\pi$ for the maxima, and positive and less than $\frac{1}{2}\pi$ for the minima.

<div style="text-align:center">

THE GIBBS' PHENOMENON FOR THE SERIES

$$2(\sin x + \tfrac{1}{3} \sin 3x + \tfrac{1}{5} \sin 5x + \ldots).$$

</div>

§ 4. From the Theorems (I)–(VI) of § 3 all the features of the Gibbs' Phenomenon for the series

$$2(\sin x + \tfrac{1}{3} \sin 3x + \tfrac{1}{5} \sin 5x + \ldots) \ldots -\pi \leqq x \leqq \pi$$

follow immediately.

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* For the values of $\int_0^{r\pi} \frac{\sin x}{x} dx$, see Bôcher, *loc. cit., Annals of Mathematics*, p. 129.

It is obvious that we need only examine the interval $0 \leqq x \leqq \pi$, and that the discontinuity occurs at $x = 0$.

For large values of n, the curve

$$y = S_n(x),$$

where $S_n(x) = 2\left(\sin x + \tfrac{1}{3}\sin 3x + \ldots + \dfrac{1}{2n-1}\sin(2n-1)x\right)$, rises at a steep gradient from the origin to its first maximum, which is very near, but above, the point $\left(0, \displaystyle\int_0^{\pi}\dfrac{\sin x}{x}dx\right)$ $\{\S\,3,\,V\}$. The curve, then, falls at a steep gradient, without reaching the axis of x $\{\S\,3,\,II\}$, to its first minimum, which is very near, but below, the point $\left(0, \displaystyle\int_0^{2\pi}\dfrac{\sin x}{x}dx\right)$ $\{\S\,3,\,VI\}$. It then oscillates above and below the line $y = \tfrac{1}{2}\pi$, the heights (and depths) of the waves continually diminishing as we proceed from $x = 0$ to $x = \tfrac{1}{2}\pi$ $\{\S\,3,\,IV\}$; and from $x = \tfrac{1}{2}\pi$ to $x = \pi$, the procedure is reversed, the curve in the interval $0 \leqq x \leqq \pi$ being symmetrical about $x = \tfrac{1}{2}\pi$ $\{\S\,3,\,I\}$.

The highest (or lowest) point of the r-th wave to the right of $x = 0$ will, for large values of n, be at a point whose abscissa is $\dfrac{r\pi}{2n}$ $\{\S\,3,\,III\}$ and whose ordinate is very nearly $\displaystyle\int_0^{r\pi}\dfrac{\sin x}{x}dx$ $\{\S\,3,\,VI\}$.

By increasing n the curve for $0 \leqq x \leqq \pi$ can be brought as close as we please to the lines

$$x = 0, \qquad 0 < y < \int_0^{\pi}\frac{\sin x}{x}dx,$$

$$0 < x < \pi, \qquad y = \frac{\pi}{2},$$

$$x = \pi, \qquad 0 < y < \int_0^{\pi}\frac{\sin x}{x}dx.$$

We may state these results more definitely as follows:

(i)   If ε is any positive number, as small as we please, there is a positive integer ν' such that

$$\left|\tfrac{1}{2}\pi - S_n(x)\right| < \varepsilon \text{ for } n \geqq \nu',\ \varepsilon \leqq x \leqq \tfrac{1}{2}\pi.$$

This follows from the uniform convergence of the Fourier's Series for $f(x)$ in an interval which does not include a discontinuity of $f(x)$.

(ii)   Since the height of the first maximum to the right of $x = 0$ tends

from above to $\int_0^\pi \frac{\sin x}{x} dx$ as n tends to infinity, there is a positive integer ν'' such that

$$0 < S_n\left(\frac{\pi}{2n}\right) - \int_0^\pi \frac{\sin x}{x} dx < \varepsilon \text{ for } n \geqq \nu''.$$

(iii)   Let ν''' be the integer next greater than $\frac{\pi}{2\varepsilon}$.   Then the abscissa of the first maximum to the right of $x=0$, for $n \geqq \nu'''$, is less than ε.

It follows from (i), (ii) and (iii) that, if ν is the greatest of the positive integers ν', ν'' and ν''', the curve $y = S_n(x)$, *for $n > \nu$*, behaves as follows:

It rises at a steep gradient from the origin to its first maximum, which is above $\int_0^\pi \frac{\sin x}{x} dx$ and within the rectangle

$$0 < x < \varepsilon, \ 0 < y < \int_0^\pi \frac{\sin x}{x} dx + \varepsilon.$$

After leaving this rectangle, in which there may be many oscillations about $y = \frac{1}{2}\pi$, it remains within the rectangle $\varepsilon < x < \pi - \varepsilon, \ \frac{1}{2}\pi - \varepsilon < y < \frac{1}{2}\pi + \varepsilon.$

Finally, it enters the rectangle

$$\pi - \varepsilon < x < \pi, \ 0 < y < \int_0^\pi \frac{\sin x}{x} dx + \varepsilon,$$

and the procedure in the first region is repeated. *

THE GIBBS' PHENOMENON FOR THE FOURIER'S SERIES IN GENERAL.

§ 5.   Let $f(x)$ be a function with an ordinary discontinuity when $x = a$, which can be expanded in a Fourier's Series in the interval $-\pi \leqq x \leqq \pi$.

Denote as usual by $f(a+0)$ and $f(a-0)$, the values towards which $f(x)$ tends as x approaches a from above or below.   It will be convenient to consider $f(a+0)$ as greater than $f(a-0)$ in the description of the curve, but this restriction is in no way necessary.

Let $\phi(x-a) = 2 \sum_1^\infty \frac{1}{(2r-1)} \sin(2r-1)(x-a)$.   Then

$$\phi(x-a) = \quad \frac{1}{2}\pi, \text{ when } a < x < \pi + a,$$
$$\phi(x-a) = -\frac{1}{2}\pi, \text{ when } -\pi + a < x < a,$$
$$\phi(+0) = \quad \frac{1}{2}\pi, \ \phi(-0) = -\frac{1}{2}\pi,$$
$$\phi(0) = \quad 0 \text{ and } \phi(x) = \phi(x+2\pi).$$

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* The cosine series

$$\frac{\pi}{4} - \left[\cos x - \frac{1}{3}\cos 3x + \frac{1}{5}\cos 5x + \ldots\right]$$

which represents 0 in the interval $0 \leqq x < \frac{\pi}{2}$ and $\frac{\pi}{2}$ in the interval $\frac{\pi}{2} < x \leqq \pi$ can be treated in the same way as the series discussed in this article.

Now put

$$\psi(x) = f(x) - \tfrac{1}{2}\{f(a+0) + f(a-0)\} - \frac{1}{\pi}\{f(a+0) - f(a-0)\}\phi(x-a),$$

and let $f(x)$, for $x=a$, be defined as $\tfrac{1}{2}\{f(a+0) + f(a-0)\}$.

Then $\psi(a+0) = \psi(a-0) = \psi(a) = 0$, and $\psi(x)$ is continuous at $x=a$.

The following distinct steps in the argument are numbered for the sake of clearness:

(i)   Since $\psi(x)$ is continuous at $x=a$ and $\psi(a)=0$, if ε is a positive number, as small as we please, a number δ exists such that

$$|\psi(x)| < \frac{\varepsilon}{4} \text{ for } |x-a| < \delta.$$

If δ is not originally less than ε, we can choose this part of δ for our interval.

(ii) $\psi(x)$ can be expanded in a Fourier's Series, this series being uniformly convergent in an interval $\alpha \leq x \leq \beta$ which includes no other discontinuity of $f(x)$ and $\phi(x-a)$ than $x=a$.

Let $s_n(x)$, $\phi_n(x-a)$ and $\sigma_n(x)$ be the sums of the terms up to and including those in $\sin nx$ and $\cos nx$ in the Fourier's Series for $f(x)$, $\phi(x-a)$ and $\psi(x)$. Then ε being the positive number of (i), as small as we please, there exists a positive integer ν' such that

$$|\sigma_n(x) - \psi(x)| < \frac{\varepsilon}{4} \text{ for } n \leq \nu' \text{ in } \alpha \leq x \leq \beta.$$

Also

$$|\sigma_n(x)| \leq |\sigma_n(x) - \psi(x)| + |\psi(x)| < \frac{\varepsilon}{4} + \frac{\varepsilon}{4} < \frac{\varepsilon}{2}$$

in $|x-a| < \delta$, if $\alpha < a-\delta < a < a+\delta < \beta$.

(iii)   Now if n is even, the first maximum in $\phi_n(x-a)$ to the right of $x=a$ is at $a + \dfrac{\pi}{n}$; and if n is odd, it is at $a + \dfrac{\pi}{n+1}$. In either case there exists a positive integer ν'' such that the height of the first maximum lies between $\displaystyle\int_0^\pi \frac{\sin x}{x} dx$ and $\displaystyle\int_0^\pi \frac{\sin x}{x} dx + \frac{\pi\varepsilon}{2\{f(a+0) - f(a-0)\}}$ for $n \geq \nu''$.

(iv)   This first maximum will have its abscissa between a and $a + \delta$, provided that $\dfrac{\pi}{n} < \delta$.

Let ν''' be the first positive integer which satisfies this inequality.

(v)   In the interval $a+\delta \leqq x \leqq \beta$, $s_n(x)$ converges uniformly to $f(x)$. herefore, there exists a positive integer $\nu^{(iv)}$ such that for $n \geqq \nu^{(iv)}$

$$|f(x) - s_n(x)| < \varepsilon \text{ in this interval.}$$

Now from the equation defining $\psi(x)$ we have

$$s_n(x) = \tfrac{1}{2}(f(a+0) + f(a-0)) + \frac{f(a+0) - f(a-0)}{\pi} \phi_n(x-a) + \sigma_n(x).$$

It follows from (i)–(v) that if ν is the first positive integer greater than ν', ν'', ν''' and $\nu^{(iv)}$, the curve $y = s_n(x)$ in the interval $a \leqq x \leqq \beta$, behaves as follows:

When $x = a$, it passes through a point whose ordinate is within $\dfrac{\varepsilon}{2}$ of $\tfrac{1}{2}(f(a+0) + f(a-0))$, and ascends at a steep gradient to its first maximum, which is at a height within ε of

$$\tfrac{1}{2}\{f(a+0) + f(a-0)\} + \frac{f(a+0) - f(a-0)}{\pi} \int_0^\pi \frac{\sin x}{x}\, dx.$$

This may be written

$$f(a+0) - \frac{f(a+0) - f(a-0)}{\pi} \int_\pi^\infty \frac{\sin x}{x}\, dx,$$

and, from Bôcher's table, referred to in § 3, we have

$$\int_\pi^\infty \frac{\sin x}{x}\, dx = -0.2811.$$

It then oscillates about $y = f(x)$ from $x = a$ to $a+\delta$, the character of the waves being determined by the function $\phi_n(x-a)$, since the term $\sigma_n(x)$ only adds a quantity less than $\dfrac{\varepsilon}{2}$ to the ordinate.

And on passing beyond $x = a+\delta$, the curve enters and remains within, the strip of width 2ε enclosing $y = f(x)$ from $x = a+\delta$ to $x = \beta$.

On the other side of the point a a similar set of circumstances can be established.

APPENDIX.

The following diagrams are the approximation curves

$$y = S_n(x)$$

of § 3 above, for $n = 1, 2, 3$ and 4. They illustrate the results (I–VI) of that section.
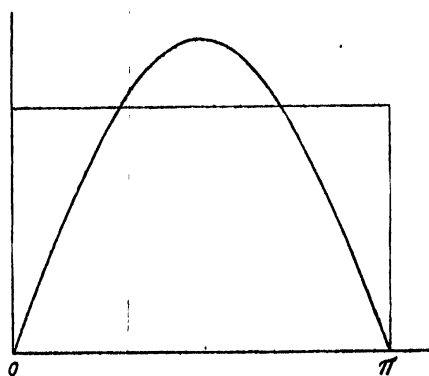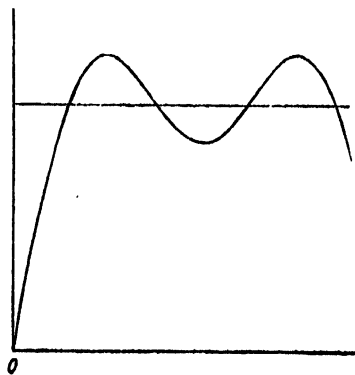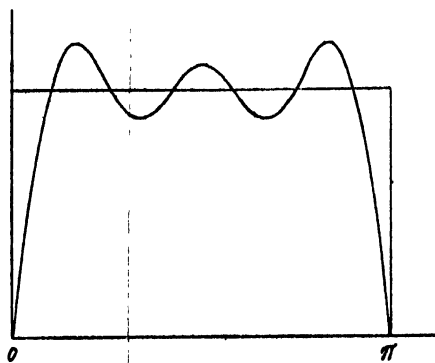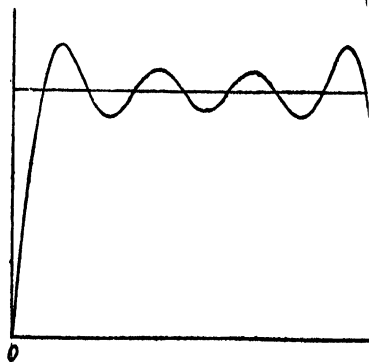
FIG. 1.

FIG. 2.

FIG. 3.

FIG. 4.

THE GREEN'S FUNCTION FOR THE EQUATION $\nabla^2 u + \kappa^2 u = 0$

(SECOND PAPER)

By H. S. CARSLAW.

Introduction.

In his recent paper on "A Class of Diffraction Problems,"[*] Macdonald deduces the solution for a source of sound between two planes cutting at any angle from the corresponding solution of the equation of potential; and he puts in analytical form his argument for the general validity of this method.

In this paper I desire to call attention to the fact that, with the same assumptions as are involved in the usual treatment of the differential equations of mathematical physics, the Green's functions, both for the equation $\nabla^2 u = 0$ and the equation $\nabla^2 u + \kappa^2 u = 0$, can be obtained immediately from an integral equation, when the region with which we are dealing is finite. The solution is as easy for the one equation as for the other in the case when the region is bounded by one sphere (or two concentric spheres), a coaxial right circular cone (or two such cones), and two axial planes; and again when the boundary consists of a circular cylinder (or two coaxial circular cylinders), two axial planes, and two planes perpendicular to the axis.

Also Fourier's method leads as readily to the solution of the equation $\nabla^2 u + \kappa^2 u = 0$ as to that of the equation $\nabla^2 u = 0$. This method has been applied by Sommerfeld to the Green's function for the former equation.[†]

For infinite regions neither Fourier's method nor that based upon the integral equation can be applied to the equation $\nabla^2 u + \kappa^2 u = 0$. For the potential problem we can, however, proceed from the finite to the infinite

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[*] *Proc. London Math. Soc.*, Ser. 2, Vol. 14, p. 410 (1915).

[†] *Jahresbericht der Deutschen Mathematiker-Vereinigung*, Bd. 21, p. 309 (1913).

region by supposing the outer boundary to move off to infinity. For this reason Macdonald's method is of special value in this large class of diffraction problems.

In my previous paper with the same title* a number of these problems were solved with the aid of contour integrals, without the assumptions above referred to. Similar rigorous proofs for a larger class of potential problems were given some years ago by Dougall.+

1. It is well known that the Green's function‡ for the equation $\nabla^2 u = 0$ appears as the kernel of a homogeneous integral equation.§

Let $K(x, y, z; x', y', z')$ be the Green's function for this equation in the region bounded by the closed surface S.

Let $\psi(x, y, z)$ be any solution of the equation

$$\nabla^2\psi + \lambda\psi = 0, \tag{1}$$

which vanishes on the surface of S, and, with its first and second differential coefficients, is finite and continuous in S.

Applying Green's theorem to the region between S and a small sphere Σ, whose centre is at (x', y', z'), we have

$$\iiint (\psi\nabla^2 K - K\nabla^2\psi)\,dx\,dy\,dz + \iint \left(\psi\frac{\partial K}{\partial n} - K\frac{\partial \psi}{\partial n}\right) d\Sigma = 0, \tag{2}$$

where $\partial/\partial n$ denotes differentiation along the outward-drawn normal to Σ.

Since the Green's function is infinite as $1/4\pi r$, when $r \to 0$, at the point (x', y', z'), if we suppose the radius of Σ to tend to zero, we obtain, from (2),

$$\psi(x', y', z') = \lambda \iiint K(x, y, z; x', y', z')\,\psi(x, y, z)\,dx\,dy\,dz, \tag{8}$$

the integration being taken through S.

A simple application of Green's theorem shows that $K(x, y, z; x', y', z')$

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* *Proc. London Math. Soc.*, Ser. 2, Vol. 18, p. 236 (1914).

† *Proc. Edinburgh Math. Soc.*, Vol. 18, p. 33 (1900).

‡ In this paper I take the infinity of the Green's function at (x', y', z') to be as $1/4\pi r$ in the potential problem (and $e^{-i\kappa r}/4\pi r$ in the wave problem). In comparing results, the factor $1/4\pi$ has to be noted. Also I take the surface condition at S to be $u = 0$. The cases $\partial u/\partial n = 0$, $\partial u/\partial n + hu = 0$ admit of the same treatment.

§ Cf. Kneser, *Die Integralgleichungen und ihre Anwendungen in der Mathematischen Physik* (Braunschweig, 1911); Heywood-Fréchet, *L'Équation de Fredholm et ses applications à la physique mathématique* (Paris, 1912).

is a symmetrical function of (x, y, z) and (x', y', z'); in other words, we have

$$K(x, y, z; x', y', z') = K(x', y', z'; x, y, z).$$

It follows, from (3), that the functions ψ are characteristic functions (*Eigenfunctionen*), and the numbers λ are characteristic numbers (*Eigenwerte*) of a homogeneous integral equation with $K(x, y, z; x', y', z')$ as its symmetrical kernel.

2. Denoting the characteristic numbers by

$$\lambda_1, \lambda_2, \ldots,$$

and the corresponding characteristic functions by

$$\psi_1, \psi_2, \ldots,$$

from Green's theorem we have at once

$$\psi_r \psi_s \, dx \, dy \, dz = 0 \quad (r \neq s), \tag{4}$$

the integration being taken through S.

And we suppose the functions normalised, so that

$$\psi^2 \, dx \, dy \, dz = 1. \tag{5}$$

If we assume that the Green's function can be expanded in the series

$$A_1 \psi_1 + A_2 \psi_2 + \ldots,$$

and that the series can be integrated term by term, we have, from (4) and (5),

$$A_r = \iiint K(x, y, z; x', y', z') \psi_r(x, y, z) \, dx \, dy \, dz$$

$$= \frac{\psi_r(x', y', z')}{\lambda_r},$$

from (3). Thus we have, subject to these assumptions,[*]

$$K(x, y, z; x', y', z') = \sum \frac{\psi_r(x, y, z) \, \psi_r(x', y', z')}{\lambda}. \tag{6}$$

3. The assumptions as to the possibility of expressing the Green's

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[*] If it can be proved that the series on the right of (6) is uniformly convergent, a fundamental theorem in the theory of integral equations allows us to equate $K(x, y, z; x', y', z')$ to the sum of the series.

function by the series of characteristic functions are practically the same as those which are made in the usual treatment of the potential problems.[*] It follows that we need not hesitate to use (6) for such problems, when the functions ψ and the corresponding numbers λ can be obtained. In my paper "On Integral Equations and the Determination of Green's Functions in the Theory of Potential,"[†] the solutions are given for all the cases mentioned in the introduction.

4. The following examples, solved by this method, will be referred to below :—

I. *The region bounded by the sphere $r = a$, the cone $\theta = \theta_0$, and the axial planes $\phi = 0$, $\phi = a$.*

Here we have

$$\psi_{\rho n m} = \sqrt{\left(\frac{2}{ar}\right)} \frac{J_{n+\frac{1}{2}}(\rho r)\, P_n^{-m\pi/a}(\mu) \sin \dfrac{m\pi}{a} \phi}{\left[\displaystyle\int_0^a r J_{n+\frac{1}{2}}^2(\rho r)\, dr \int_{\mu_0}^1 \left[P_\phi^{-m\pi/a}(\mu)\right]^2 d\mu\right]^{\frac{1}{2}}},$$

where m is any positive integer,

            n is any positive root of $P_n^{-m\pi/a}(\mu_0) = 0$,

            ρ is any positive root of $J_{n+\frac{1}{2}}(\rho a) = 0$,

and $\lambda = \rho^2$.

It follows, from (6), that the Green's function $K(r, \theta, \phi\,;\, r', \theta', \phi')$ is given by[‡]

$$\frac{2}{a\sqrt{(rr')}} \sum_\rho \sum_n \sum_m \frac{J_{n+\frac{1}{2}}(\rho r)\, J_{n+\frac{1}{2}}(\rho r')\, P_n^{-m\pi/a}(\mu)\, P_n^{-m\pi/a}(\mu') \sin \dfrac{m\pi}{a} \phi \sin \dfrac{m\pi}{a} \phi'}{\rho^2 \displaystyle\int_0^a r J_{n+\frac{1}{2}}^2(\rho r)\, dr \int_{\mu_0}^1 \left[P_n^{-m\pi/a}(\mu)\right]^2 d\mu}. \quad (7)$$

II. *The region bounded by the spheres $r = a$, $r = b$, the cone $\theta = \theta_0$, and the axial planes $\phi = 0$, $\phi = a$.*

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[*] Cf. Macdonald, *Proc. London Math. Soc.*, Ser. 1, Vol. XXVI, p. 156 (1895).

[†] *Proc. Edinburgh Math. Soc.*, Vol. 31, p. 71 (1913).

[‡] *Loc. cit.*, p. 86. The Green's function for the wedge, which Macdonald obtains in his last paper, will be found here under Corollary (ii), deduced from the above by making $a \to \infty$ and $\mu_0 \to -1$.

Here we have

$$\psi_{\rho n m} = \sqrt{\left(\frac{2}{a r}\right)} \frac{U_{n+\frac{1}{2}}(\rho r)\, P_n^{-m\pi/a}(\mu) \sin \dfrac{m\pi}{a}\, \phi}{\left[\displaystyle\int_a^b r\, U_{n+\frac{1}{2}}^2(\rho r)\, dr \int_{\mu_0}^1 \left[P_n^{-m\pi/a}(\mu)\right]^2 d\mu\right]^{\frac{1}{2}}},$$

where m is any positive integer,

   n is any positive root of $P_n^{-m\pi/a}(\mu_0) = 0$,

$$U_n(x) = J_n(x)\, K_n(ib) - J_n(b)\, K_n(ix),*$$

   ρ is any positive root of $U_n(\rho a) = 0$,

and $\lambda = \rho^2$.

It follows, from (6), that the Green's function is given by

$$\frac{2}{a \sqrt{(rr')}} \sum_\rho \sum_n \sum_m \frac{U_{n+\frac{1}{2}}(\rho r)\, U_{n+\frac{1}{2}}(\rho r')\, P_n^{-m\pi/a}(\mu)\, P_n^{-m\pi/a}(\mu') \sin \dfrac{m\pi}{a}\phi \sin \dfrac{m\pi}{a}\phi'}{\rho^2 \displaystyle\int_a^b r\, U_{n+\frac{1}{2}}^2(\rho r)\, dr \int_{\mu_0}^1 \left[P_n^{-m\pi/a}(\mu)\right]^2 d\mu}. \qquad (8)$$

5. In my paper with the same title,† I pointed out that the equation $\nabla^2 u + \kappa^2 u = 0$ can be treated in a similar way. But I did not enter into details, as my object in that paper was to obtain the Green's functions by a rigorous method; that is, without the assumptions involved in the treatment given in the preceding sections.

If $K(x, y, z ; x', y', z')$ is the solution of the equation $\nabla^2 u + \kappa^2 u = 0$ which vanishes at the surface S, and is finite and continuous, as also its first and second differential coefficients, inside S, except at (x', y', z'), where it becomes infinite as $e^{-i\kappa r}/4\pi r$, where $r \to 0$, then $K(x, y, z ; x', y', z')$ is the symmetrical kernel of a homogeneous integral equation.

Indeed, if $\psi(x, y, z)$‡ is a solution of the equation

$$\nabla^2 \psi + (\lambda + \kappa^2)\psi = 0, \qquad (9)$$

which vanishes at the surface of S, and is finite and continuous, as also

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  * $K_n(ix)$ as usual stands for $\dfrac{\pi}{2 \sin n\pi}\, e^{-\frac{1}{2}n\pi i} \left[J_{-n}(x) - e^{n i \pi} J_n(x)\right]$.

  † *Loc. cit.*, p. 237.

  ‡ The value $\lambda = 0$ is excluded, since we assume that κ^2 does not belong to one of the normal modes of vibration.

its first and second differential coefficients, inside S, we have

$$\psi(x', y', z') = \lambda \iiint K(x, y, z \; ; \; x', y', z') \, \psi(x, y, z) \, dx \, dy \, dz, \qquad (10)$$

the integration being taken through S.

And with the same notation as in § 2, we have

$$\psi_r \psi_s \, dx \, dy \, dz = 0 \quad (r \neq s),$$

$$\iiint \psi_r^2 \, dx \, dy \, dz = 1.$$

Also, if we assume that $K(x, y, z \; ; \; x', y', z')$ can be expanded in the series
$$A_1 \psi_1 + A_2 \psi_2 + \ldots,$$

and that the series can be integrated term by term, we have

$$A_r = \iiint K(x, y, z \; ; \; x', y', z') \, \psi_r(x, y, z) \, dx \, dy \, dz$$

$$= \frac{\psi_r(x', y', z')}{\lambda_r}.$$

Thus we have, as before,

$$K(x, y, z \; ; \; x', y', z') = \sum_r \frac{\psi_r(x, y, z) \, \psi_r(x', y', z')}{\lambda_r}. \qquad (11)$$

6. From (11) the Green's functions for the cases treated in § 4 (and other similar cases) can be written down :—

1. *The region bounded by the sphere* $r = a$, *the cone* $\theta = \theta_0$, *and the axial planes* $\phi = 0$, $\phi = a$.

The Green's function* is given by

$$\frac{2}{a\sqrt{(rr')}} \sum_\rho \sum_n \sum_m \frac{J_{n+\frac{1}{2}}(\rho r) \, J_{n+\frac{1}{2}}(\rho r') \, P_n^{-m\pi/a}(\mu) \, P_n^{-m\pi/a}(\mu') \sin \frac{m\pi}{a} \phi \sin \frac{m\pi}{a} \phi'}{(\rho^2 - \kappa^2) \displaystyle\int_0^a r J_{n+\frac{1}{2}}^2(\rho r) \, dr \int_{\mu_0}^1 [P_n^{-m\pi/a}(\mu)]^2 \, d\mu}, \qquad (12)$$

with the same notation as in § 4, I.

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* The solution for the region bounded by the sphere, and the axial planes, is obtained by letting $\mu_0 \rightarrow -1$, as in my paper on potential (*loc. cit.*, §§ 11, 13).

II. *The region bounded by the spheres $r = a$, $r = b$, the cone $\theta = \theta_0$, and the axial planes $\phi = 0$, $\phi = a$.*

The Green's function is given by

$$\frac{2}{a\sqrt{(rr')}} \sum_{\rho} \sum_{n} \sum_{m} \frac{U_{n+\frac{1}{2}}(\rho r)\, U_{n+\frac{1}{2}}(\rho r')\, P_n^{-m\pi/a}(\mu)\, P_n^{-m\pi/a}(\mu')\, \sin\frac{m\pi}{a}\phi\, \sin\frac{m\pi}{a}\phi'}{(\rho^2 - \kappa^2)\displaystyle\int_a^b r U_{n+\frac{1}{2}}^2(\rho r)\, dr \int_{\mu_0}^1 [P_n^{-m\pi/a}(\mu)]^2\, d\mu}, \quad (13)$$

with the same notation as in § 4, II.

7. The results of §§ 4, 6 can be simplified with the aid of the following theorems on Bessel's functions :—

I. *Let n be a given positive number, and $\rho_1, \rho_2, \ldots$ the positive roots of the equation*
$$J_n(\rho a) = 0.$$
Then we have

$$\sum_{\rho} \frac{J_n(\rho r)\, J_n(\rho r')}{\rho^2 \displaystyle\int_0^a r J_r^2(\rho r)\, dr} = \frac{1}{2n}\left(\frac{r}{a}\right)^n \left\{\left(\frac{a}{r'}\right)^n - \left(\frac{r'}{a}\right)^n\right\} \quad (0 < r < r')$$

$$= \frac{1}{2n}\left(\frac{r'}{a}\right)^n \left\{\left(\frac{a}{r}\right)^n - \left(\frac{r}{a}\right)^n\right\} \quad (r' < r < a). \quad (14)$$

II. *Let n be a given positive number, and $\rho_1, \rho_2, \ldots$ the positive roots of the equation*
$$U_n(\rho a) = J_n(\rho a)\, K_n(i\rho b) - J_n(\rho b)\, K_n(i\rho a) = 0 \quad (0 < a < b).$$
Then we have

$$\sum_{\rho} \frac{U_n(\rho r)\, U_n(\rho r')}{\rho^2 \displaystyle\int_a^b r U_n^2(\rho r)\, dr} = \frac{\frac{1}{2n}\left\{\left(\frac{r}{a}\right)^n - \left(\frac{a}{r}\right)^n\right\}\left\{\left(\frac{b}{r'}\right)^n - \left(\frac{r'}{b}\right)^n\right\}}{\left(\frac{b}{a}\right)^n - \left(\frac{a}{b}\right)^n} \quad (a < r < r')$$

$$= \frac{\frac{1}{2n}\left\{\left(\frac{r'}{a}\right)^n - \left(\frac{a}{r'}\right)^n\right\}\left\{\left(\frac{b}{r}\right)^n - \left(\frac{r}{b}\right)^n\right\}}{\left(\frac{b}{a}\right)^n - \left(\frac{a}{b}\right)^n} \quad (r' < r < b). \quad (15)$$

III. *Let n be a given positive number, and $\rho_1, \rho_2, \ldots$ the positive roots of the equation*
$$J_n(\rho a) = 0,$$

while κ^2 is not equal to ρ^2. Then we have

$$\sum_\rho \frac{J_n(\rho r)\, J_n(\rho r')}{(\rho^2 - \kappa^2) \displaystyle\int_0^a r J_n^2(\rho r)\, dr} = e^{\frac{1}{2}n i\pi}\frac{J_n(\kappa r)}{J_n(\kappa a)}\left\{ J_n(\kappa a)\, K_n(i\kappa r') - J_n(\kappa r')\, K_n(i\kappa a)\right\}$$

$$(0 < r < r')$$

$$= e^{\frac{1}{2}n i\pi}\frac{J_n(\kappa r')}{J_n(\kappa a)}\left\{ J_n(\kappa a)\, K_n(i\kappa r) - J_n(\kappa r)\, K_n(i\kappa a)\right\}$$

$$(r' < r < b). \quad (16)$$

IV. *Let n be a given positive number, and ρ_1, ρ_2, ... the positive roots of the equation*

$$U_n(\rho a) = J_n(\rho a)\, K_n(i\rho b) - J_n(\rho b)\, K_n(i\rho a) = 0 \quad (0 < a < b).$$

Then, κ^2 not being equal to ρ^2, we have

$$\sum_\rho \frac{U_n(\rho r)\, U_n(\rho r')}{(\rho^2 - \kappa^2)\displaystyle\int_a^b r U_n^2(\rho r)\, dr}$$

$$= \frac{e^{\frac{1}{2}n i\pi}\left\{ J_n(\kappa r)\, K_n(i\kappa a) - J_n(\kappa a)\, K_n(i\kappa r)\right\}\left\{ J_n(\kappa r')\, K_n(i\kappa b) - J_n(\kappa b)\, K_n(i\kappa r')\right\}}{J_n(\kappa a)\, K_n(i\kappa b) - J_n(\kappa b)\, K_n(i\kappa a)}$$

$$(a < r < r')$$

$$= \frac{e^{\frac{1}{2}n i\pi}\left\{ J_n(\kappa r')\, K_n(i\kappa a) - J_n(\kappa a)\, K_n(i\kappa r')\right\}\left\{ J_n(\kappa r)\, K_n(i\kappa b) - J_n(\kappa b)\, K_n(i\kappa r)\right\}}{J_n(\kappa a)\, K_n(i\kappa b) - J_n(\kappa b)\, K_n(i\kappa a)}$$

$$(r' < r < b). \quad (17)$$

The first of these theorems was proved by Kneser (*Integralgleichungen*, § 27). The second follows in the same way. The third was proved by Kneser.[*] The fourth follows in the same way.

8. Using 7, I and II, the Green's function for the potential problems of § 4 reduce to :—

$$\text{I}: \ \frac{2}{a\sqrt{(rr')}}\sum_n\sum_m\frac{1}{2n+1}\ \frac{\left(\dfrac{r}{a}\right)^{n+\frac{1}{2}}\left\{\left(\dfrac{a}{r'}\right)^{n+\frac{1}{2}} - \left(\dfrac{r'}{a}\right)^{n+\frac{1}{2}}\right\}}{\displaystyle\int_{\mu_0}^1 [P_n^{-m\pi/a}(\mu)]^2\, d\mu}$$

$$\times P_n^{-m\pi/a}(\mu)\, P_n^{-m\pi/a}(\mu')\sin\frac{m\pi}{a}\phi\,\sin\frac{m\pi}{a}\phi', \quad (18)$$

* *Math. Ann.*, Bd. 63, p. 510 (1907).

when $0 < r < r'$.

II : $\dfrac{2}{a\sqrt{(rr')}} \sum\limits_n \sum\limits_m \dfrac{\dfrac{1}{2n+1}\left\{\left(\dfrac{r}{a}\right)^{n+\frac{1}{2}}-\left(\dfrac{a}{r}\right)^{n+\frac{1}{2}}\right\}\left\{\left(\dfrac{b}{r'}\right)^{n+\frac{1}{2}}-\left(\dfrac{r'}{b}\right)^{n+\frac{1}{2}}\right\}}{\left\{\left(\dfrac{b}{a}\right)^{n+\frac{1}{2}}-\left(\dfrac{a}{b}\right)^{n+\frac{1}{2}}\right\}\displaystyle\int_{\mu_0}^{1}[P_n^{-m\pi/a}(\mu)]^2\,d\mu}$

$$\times P_n^{-m\pi/a}(\mu)\,P_n^{-m\pi/a}(\mu')\sin\frac{m\pi}{a}\phi\sin\frac{m\pi}{a}\phi', \quad (19)$$

where $a < r < r'$.

These results are completed by interchanging r and r', when $r' < r < a$ in I, and $r' < r < b$ in II.

9. Also using § 7, III and IV, the Green's functions for the equation $\nabla^2 u + \kappa^2 u = 0$ in the regions of § 6, I and II, reduce to :—

I : $\dfrac{2}{a\sqrt{(rr')}} \sum\limits_n \sum\limits_m e^{\frac{1}{2}(n+\frac{1}{2})i\pi}\dfrac{J_{n+\frac{1}{2}}(\kappa r)}{J_{n+\frac{1}{2}}(\kappa a)}\{J_{n+\frac{1}{2}}(\kappa a)\,K_{n+\frac{1}{2}}(i\kappa r')-J_{n+\frac{1}{2}}(\kappa r')\,K_{n+\frac{1}{2}}(i\kappa a)\}$

$$\times \dfrac{P_n^{-m\pi/a}(\mu)\,P_n^{-m\pi/a}(\mu')}{\displaystyle\int_{\mu_0}^{1}[P_n^{-m\pi/a}(\mu)]^2\,d\mu}\sin\frac{m\pi}{a}\phi\sin\frac{m\pi}{a}\phi', \quad (20)$$

when $0 < r < r'$.

II : $\dfrac{2}{a\sqrt{(rr')}} \sum\limits_n \sum\limits_m e^{\frac{1}{2}(n+\frac{1}{2})i\pi}\dfrac{\{J_{n+\frac{1}{2}}(\kappa r)\,K_{n+\frac{1}{2}}(i\kappa a)-J_{n+\frac{1}{2}}(\kappa a)\,K_{n+\frac{1}{2}}(i\kappa r)\}}{J_{n+\frac{1}{2}}(\kappa a)\,K_{n+\frac{1}{2}}(i\kappa b)-J_{n+\frac{1}{2}}(\kappa b)\,K_{n+\frac{1}{2}}(i\kappa a)}$
$$\times\{J_{n+\frac{1}{2}}(\kappa r')\,K_{n+\frac{1}{2}}(i\kappa b)-J_{n+\frac{1}{2}}(\kappa b)\,K_{n+\frac{1}{2}}(i\kappa r')\}$$

$$\times \dfrac{P_n^{-m\pi/a}(\mu)\,P_n^{-m\pi/a}(\mu')}{\displaystyle\int_{\mu_0}^{1}[P_n^{-m\pi/a}(\mu)]^2\,d\mu}\sin\frac{m\pi}{a}\phi\sin\frac{m\pi}{a}\phi', \quad (21)$$

when $a < r < r'$.

These results are completed by interchanging r and r', when $r' < r < a$ in I, and $r' < r < b$ in II.

Using the limiting values for the Bessel's functions $J_n(x)$ and $K_n(ix)$ as $x \to 0$, it will be found that the results I and II of this section reduce, when $\kappa \to 0$ to those of § 8, I and II.

This is an independent verification of the formulæ (20) and (21).

10. In his discussion of the problem of the diffraction of electric waves by a perfectly conducting right circular cone, Macdonald determined the constants in his series from the fact that these constants must be identical

with the constants in the solution of the corresponding potential problem, when both series are expressed in terms of the appropriate harmonic functions.

In his recent communication to these *Proceedings*, he puts in analytical form his argument for the general validity of this method.

In the solutions of §§ 8, 9 above, Macdonald's theorem holds.

One of the difficulties in the treatment of the equation $\nabla^2 u + \kappa^2 u = 0$ has been that we cannot proceed from the bounded region to the infinite region, as in the case of potential; *e.g.* by letting the radius of the outer sphere tend to infinity in § 6, II. We have to make sure that there is no reflection at infinity. With Macdonald's method the solutions for the diffraction problems in infinite regions are obtained at once from those of the corresponding potential problems.

DIFFRACTION OF WAVES BY A WEDGE OF ANY ANGLE

By H. S. CARSLAW.

THE solution of the problem of diffraction by a wedge of any angle in the two dimensional cases of plane waves and a line-source, and the three dimensional case of a point-source, is due to Macdonald.[†] The case of a point-source has been treated differently by Bromwich.[‡] If I understand him aright, he believes that Sommerfeld's methods are only of use in the case of the half-plane, or wedge of angle 2π.[§] As a matter of fact Sommerfeld himself showed how, by his methods, the solution could be obtained for a wedge of angle $n\pi/m$ (m, n being positive integers), a Riemann's surface of n sheets being used, and he pointed out that, when the angle of the wedge is not commensurable with π, a Riemann's surface of an infinite number of sheets can be employed in the same way.[‖] Recently Wiegrefe has given a very complete discussion of the diffraction of plane waves by a wedge of any angle by this method, and he has also given the formal solution for a line-source and point-source.[¶] In §§ 2, 3 below, a statement of Sommerfeld's method will be found.

In this paper I also show that the three problems solved by Macdonald by his method of deducing the solution in series for the wave equation from the corresponding solution in series for the equation of potential can be treated by the modification of Sommerfeld's work, employed by me in dealing with Green's functions for the Wedge of any

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Angle in the Conduction of Heat.* In my method, for the wedge of any angle β, a periodic solution of period 2β is required, and no use is made of Riemann's surfaces.

Also I give, by the same method, the solution for the case of plane waves when the direction in which they are travelling is not perpendicular to the edge of the wedge. This problem, for the wedge of any angle,† is here solved for the first time.

$$\text{THE EQUATION } \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \kappa^2 u = 0.$$

PLANE WAVES.

Solution of Period $2n\pi$.

1. In my former paper‡ the fundamental solution

$$u_0 = e^{i\kappa r \cos(\theta - \theta')},$$

which represents the disturbance due to plane waves coming from the direction θ', is transformed into the integral

$$\frac{1}{2\pi} \int e^{i\kappa r \cos(a-\theta)} \frac{e^{ia}}{e^{ia} - e^{i\theta'}} \, da,$$

over the path (A) of Fig. 1, in the a-plane. These two curves are supposed symmetrical and asymptotic to the lines $\pm \pi + \theta$ in the shaded intervals. These shaded intervals denote parts of the a-plane in which the imaginary part of $\cos(a - \theta)$ is positive. In this transformation θ' is supposed to lie between $-\pi + \theta$ and $\pi + \theta$. Any path consisting of two such parts, beginning in the shaded part at infinity to the right of θ and ending in the shaded part to the left of θ, without cutting the real axis, will give the same integral.

An expression of period $2n\pi$, n being a positive integer, was then obtained, by taking the following integral over the same path (A) in the

* *Proc. London Math. Soc*, Ser. 2, Vol. 8 (1910), p. 365. This paper will be referred to below as (G.F.).

† The case of Oblique Incidence on the Semi-Infinite Plane has been treated by me previously, cf. *Proc. Edinburgh Math. Soc.*, Vol. 19 (1901), p. 71.

‡ *Proc. London Math. Soc.*, Ser. 1, Vol. xxx (1898), p. 121. This paper on "Multiform Solutions" will be referred to below as (M.S.).

α-plane :—

$$u = \frac{1}{2n\pi} \int e^{i\kappa r \cos(\alpha - \theta)} \frac{e^{i\alpha/n}}{e^{i\alpha/n} - e^{i\theta'/n}} \, d\alpha. \tag{1}$$

The following properties of the expression in (1) were proved :—

(i) It is a solution of the differential equation.

(ii) It is periodic in θ, of period $2n\pi$.

(iii) It is finite and continuous.

(iv) As $r \to \infty$, $u \to u_0$ when $|\theta - \theta'| < \pi$, and $u \to 0$ when $\pi < |\theta - \theta'| < 2n\pi$.
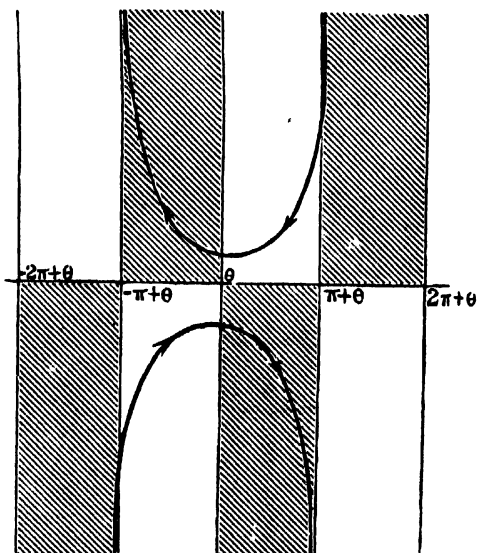
FIG. 1.—The path (A) in the v-plane. Breadth of strip, π.

Now put $\alpha - \theta = \alpha'$ in (1) and we obtain

$$u = \frac{1}{2n\pi} \int e^{i\kappa r \cos \alpha'} \frac{e^{i(\alpha' + \theta)/n}}{e^{i(\alpha' + \theta)/n} - e^{i\theta'/n}} \, d\alpha',$$

over the path (A') of Fig. 2, in the α'-plane.

In the lower part of the path change the sign of α', and we bring it to

the upper part, and have, finally,

$$u = \frac{1}{2n\pi} \int e^{i\kappa r \cos \alpha'} \left(\frac{e^{i(\alpha'+\theta)/n}}{e^{i(\alpha'+\theta)/n} - e^{i\theta'/n}} - \frac{e^{i(-\alpha'+\theta)/n}}{e^{i(-\alpha'+\theta)/n} - e^{i\theta'/n}} \right) d\alpha'$$

$$= \frac{i}{2n\pi} \int e^{i\kappa r \cos \alpha'} \frac{\sin \dfrac{\cdot}{n}}{\cos \dfrac{\alpha'}{n} - \cos \dfrac{\theta-\theta'}{n}} d\alpha', \tag{2}$$

over the *upper* part of the path (A') in the α'-plane, or any similar path not cutting the real axis, and beginning at infinity in the shaded part to the right of the origin and ending at infinity in the shaded part to the left.
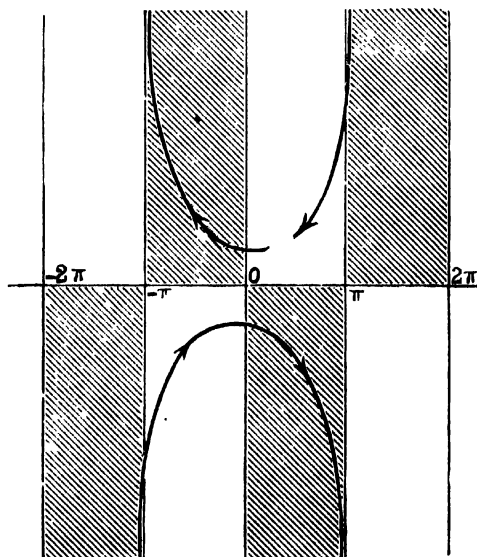
FIG. 2.—Breadth of strip, π; the path (A') in the α'-plane.

2. *Sommerfeld's solution for the wedge of angle $n\pi/m$ (m and n being positive integers).*

Sommerfeld's method of solution for the case of plane waves and the wedge of any angle $n\pi/m$ (m and n being positive integers) is to form the sums :—

$$U_1 = u(\theta') + u\left(\theta' + 2\frac{n\pi}{m}\right) + u\left(\theta' + 4\frac{n\pi}{m}\right) + \dots \text{ to } m \text{ terms},$$

and $U_2 = u(-\theta') + u\left(-\theta' + 2\dfrac{n\pi}{m}\right) + u\left(-\theta' + 4\dfrac{n\pi}{m}\right) + \ldots$ to m terms,

denoting the periodic solution of period $2n\pi$ given in § 1 (2) by $u(\theta')$.

The solution of the physical problem is given by

$$u = U_1 \mp U_2, \quad 0 < \theta < \frac{n\pi}{m}, \quad 0 < \theta' < \frac{n\pi}{m},$$

the negative or positive sign being chosen according as $u = 0$ or $\partial u/\partial n = 0$ is the boundary condition.

A simple piece of trigonometry reduces this to the form

$$u = \frac{im}{2n\pi}\int e^{i\kappa r\cos a'}\left\{\frac{\sin\dfrac{m}{n}\,a'}{\cos\dfrac{m}{n}\,a' - \cos\dfrac{m}{n}(\theta-\theta')} \mp \frac{\sin\dfrac{m}{n}\,a'}{\cos\dfrac{m}{n}\,a' - \cos\dfrac{m}{n}(\theta+\theta')}\right\}\,da',$$

$$(3)$$

over the upper part of the path (A') of Fig. 2 in the a'-plane.

Sommerfeld speaks of the terms in U_1 and U_2 as the images of $u(\theta)$ in a Riemann's surface of n sheets. He reached the solution for the wedge of any angle by letting n tend to infinity. His method will be described in the next section.*

3. *Sommerfeld's solution for the wedge of any angle β.*

Consider the function defined in § 1 by the equation

$$u = \frac{1}{2n\pi}\int e^{i\kappa r\cos(a-\theta)}\frac{e^{ia/n}}{e^{ia/n} - e^{i\theta'/n}}\,da,$$

over the path (A) of Fig. 1.

Let n tend to infinity, and we are brought to a solution of the differential equation in the form

$$u = \frac{1}{2i\pi}\int e^{i\kappa r\cos(a-\theta)}\frac{da}{a-\theta'},$$

over the path (A).

This function vanishes at $r = \infty$, except when θ lies in the interval

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* This method is referred to in various passages of Sommerfeld's papers on this subject. Cf., for example, p. 38 of the paper in Schlömilch's *Zeitschrift*, cited in the introduction. See also Wiegrefe (*loc. cit.*, p. 456).

$|\theta-\theta'| < \pi$, and when θ does lie in this interval we have $u = e^{i\kappa r \cos(\theta-\theta')}$ at $r = \infty$.

As before, this solution reduces to

$$u = \frac{1}{2i\pi} \int e^{i\kappa r \cos a'} \frac{da'}{a'+\theta-\theta'},$$

over the path (A′) of Fig. 2 in the a'-plane.

And, finally, by changing the sign of a' in the lower part of this path, as in § 1, we reduce the solution to the form

$$u = \frac{1}{2i\pi} \int e^{i\kappa r \cos a'} \left(\frac{1}{a'+\theta-\theta'} + \frac{1}{a'-\theta+\theta'} \right) da'$$

$$= \frac{1}{2i\pi} \int e^{i\kappa r \cos a'} \frac{2a'}{a'^2-(\theta-\theta')^2} da', \tag{4}$$

over the *upper* part only by the path (A′) of Fig. 2.

Denote this solution (4) by $u(\theta')$, remarking that it must not be confused with the previous function of § 2, for which the same symbol was used.

Now add to this the solutions which correspond to waves in directions

$$\theta' \pm 2\beta, \quad \theta' \pm 4\beta, \quad \ldots.$$

Then we have, in place of U_1 of § 2, an infinite series

$$U_1 = \sum_{s=-\infty}^{\infty} u(\theta'+2s\beta)$$

$$= \frac{1}{2i\pi} \int e^{i\kappa r \cos a} \sum_{-\infty}^{\infty} \frac{2a'}{a'^2-(\theta-\theta'-2s\beta)^2} da',$$

over the *upper* part only of the path (A′) of Fig. 2.

But we know that

$$\frac{\dfrac{\pi}{\beta} \sin \dfrac{\pi}{\beta} a'}{\cos \dfrac{\pi}{\beta} a' - \cos \dfrac{\pi}{\beta} (\theta-\theta')} = -\sum_{-\infty}^{\infty} \frac{2a'}{a'^2-(\theta-\theta'-2s\beta)^2}.$$

Therefore $\quad U_1 = \dfrac{i}{2\beta} \int e^{i\kappa r \cos a'} \dfrac{\sin \dfrac{\pi}{\beta} a'}{\cos \dfrac{\pi}{\beta} a' - \cos \dfrac{\pi}{\beta} (\theta-\theta')} da', \tag{5}$

over the *upper* part only of the path (A′).

Similarly, $U_2 = \overset{\infty}{\Sigma}\, u(-\theta' + 2s\beta)$

$$= \frac{1}{2\beta} \int e^{i\kappa r\, c} \frac{\sin \frac{\pi}{\beta}\, a'}{\cos \frac{\pi}{\beta}\, a' - \cos \frac{\pi}{\beta}\,(\theta + \theta')}\, da,$$

over the *upper* part only of the path (A').

Also the solution of the physical problem is given by

$$u = U_1 \mp U_2, \quad 0 < \theta < \beta, \quad 0 < \theta' < \beta,$$

as before.[*]

4. The solution of period 2β given in (5) can also be obtained, as in §§ 6, 8 and 10 below, by starting from the integral

$$\frac{1}{2\beta} \int e^{i\kappa r \cos(a-\theta)} \frac{e^{i\pi a/\beta}}{e^{i\pi a/\beta} - e^{i\pi \theta'/\beta}}\, da, \tag{6}$$

over the path (A) of Fig. 1.

It can be reduced to a series of Bessel's functions as in ((G. F.) § 2.

Then we have[†]

$$U_1 = \frac{\pi}{\beta} \left(J_0(\kappa r) + 2 \overset{\infty}{\underset{1}{\Sigma}}\, e^{i s\pi^2/2\beta} J_{s\pi/\beta}(\kappa r) \cos s\pi(\theta - \theta')/\beta \right), \tag{7}$$

which agrees, when $\beta = \pi$, with the series for $e^{i\kappa r \cos(\theta-\theta')}$, namely

$$J_0(\kappa r) + 2 \overset{\infty}{\underset{1}{\Sigma}}\, e^{i s\pi/2} J_s(\kappa r) \cos s(\theta - \theta').$$

For the case in which $u = 0$ at the surface of the wedge, we have

$$u = \frac{4\pi}{\beta} \overset{\infty}{\underset{1}{\Sigma}}\, e^{i s\pi^2/2\beta} J_{s\pi/\beta}(\kappa r) \sin s\pi\theta/\beta \sin s\pi\theta'/\beta. \tag{8}$$

5. *A line-source at* (r', θ').

We suppose the line-source at (r', θ') parallel to the edge of the wedge.

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[*] Cf. Macdonald, *Electric Waves*, p. 192.

[†] Cf. Sommerfeld, *Math. Ann.*, Vol. 47 (1896), p. 346; if the solutions corresponding to his expression for *u* at the end of § 5 (3) are taken for θ', $\theta' + 2n\pi/m$, etc., to m terms, and summed, the result agrees with the above when $\beta = n\pi/m$.

In this case we start with the fundamental solution

$$u_0 = K_0(i\kappa R),$$

where $$R^2 = r^2 + r'^2 - 2rr'\cos(\theta - \theta').$$

This is transformed into the following integral in the a-plane,

$$\frac{1}{2\pi}\int K_0(i\kappa R)\,\frac{e^{ia}}{e^{ia} - e^{i\theta'}}\,da,$$

the path being the two symmetrical curves* of Fig. 3. This path we shall again refer to as the path (A).
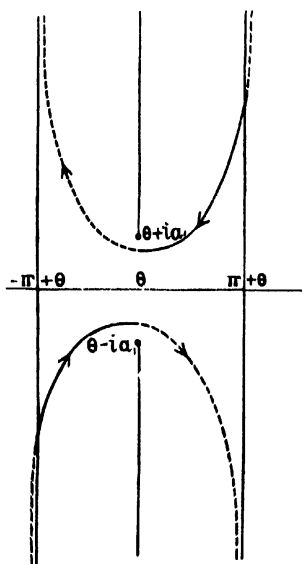
Fig. 3.—Breadth of strip. 2π; the path (A) in the a-plane.

In this integral, R stands for $\sqrt{[r^2 + r'^2 - 2rr'\cos(a - \theta)]}$.

In making this transformation of u_0, we require cuts in the a-plane

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* In my former paper (M.S.) some modification is needed in Fig. 6. As drawn, it represents the case when R is taken as negative on the real axis.

In this paper I use $K_0(ix)$ for the required Bessel's function of the second kind. With the notation now customary,

$$K_n(ix) = \frac{\pi}{2\sin n\pi}\,e^{-\frac{1}{2}in\pi}\,[J_{-n}(x) - e^{in\pi}J_n(x)].$$

from the branch points of R parallel to the imaginary axis. These branch points are given by

$$a = \theta + 2s\pi \pm ia_1,$$

where

$$\cosh a_1 = \frac{r^2 + r'^2}{2rr'},$$

and s is zero or any positive or negative integer.

The points $\theta \pm ia_1$ are to lie within the path (A) on the right-hand as we pass along this path.

The value of R is fixed in the a-plane, when the cuts are made, if we agree that it is to be positive, say, on the real axis. In this case the dotted parts of the path (A) of Fig. 3 denote points at which the imaginary part of R is negative. In the standard diagram (Fig. 3) the curves are supposed asymptotic to $\pm \pi + \theta$, but the upper curve, for example, could begin at infinity between $\pi + \theta$ and $2\pi + \theta$, and end at infinity between $-\pi + \theta$ and θ.

6. Consider the expression

$$u = \frac{1}{2\beta} \int K_0(i\kappa R) \frac{e^{i\pi a/\beta}}{e^{i\pi a/\beta} - e^{i\pi r''/\beta}} \, du, \tag{9}$$

over the path (A) of Fig. 3 in the a-plane.

This expression has the following properties :—

(i) It is a solution of the differential equation.

(ii) It is periodic in θ, of period 2β. A change in θ, e.g. from θ to ϕ, simply translates the path along the real axis of a, and the term $K_0(i\kappa R)$ is unaltered. Further, if the change in θ is equal to $2s\beta$, where s is any positive or negative integer, the other factor of the integrand is unaltered.

(iii) The choice of the path (A) makes the expression finite and continuous when a_1 is not zero, i.e. when r is not equal to r'.

This follows from the approximation for $K_0(ix)$, namely

$$\sqrt{\left(\frac{\pi}{2x}\right)} \, e^{-i(x+\pi/4)},$$

when $|x|$ is large.*

To learn the behaviour of the expression as $a_1 \to 0$, we note that the

* Cf. Nielsen, *Handbuch d. Th. d. Cylinderfunktionen* (1904), Ch. ɪ.

path (A) may be replaced by rectilinear parts along which the imaginary part of R is negative [cf. (M.S.), pp. 128–9, and 138–9, also (G.F.), p. 367], and circuits round the points $\theta' + 2s\beta$, s being zero or any positive or negative integer, lying within $\pm \pi + \theta$. The straight lines give convergent integrals. The circuits round $\theta' + 2s\beta$ give for each

$$K_0 \left[i\kappa \sqrt{\{ r^2 + r'^2 - 2rr' \cos(\theta - \theta' - 2s\beta) \}} \right],$$

and these terms can be interpreted as images of the source. They are finite, since $r \gtrless r'$.

As $a_1 \to 0$, the same argument holds, but one of the circuits will now give an infinity of the order $K_0(ix)$ when $x \to 0$, if $\theta = \theta' + 2s\beta$, s being zero or any positive or negative integer.

Thus, if the range of θ, in the space with which we are concerned, is $0 < \theta < \beta$, and if $0 < \theta' < \beta$, there will be one point (r', θ'), and only one, at which the expression is infinite.

Also, if we take the solution corresponding to $-\theta'$, where $0 < \theta' < \beta$, there will be no infinity in the region $0 < \theta < \beta$ for it.

When $r \to \infty$, $u \to 0$, and there are no terms corresponding to waves reflected at infinity. This follows from the argument of (iii) above.

The expression in (9) is reduced as in § 1 to

$$u(\theta') = \frac{i}{2\beta} \int K_0(i\kappa R) \, \frac{\sin \dfrac{\pi}{\beta} a'}{\cos \dfrac{\pi}{\beta} a' - \cos \dfrac{\pi}{\beta}(\theta - \theta')} \, da', \qquad (10)$$

over the *upper* part of the path (A') of Fig. 4 in the a'-plane, or an equivalent path.

In (10), $R = \sqrt{(r^2 + r'^2 - 2rr' \cos a')}.$

It can further be reduced to the series

$$u(\theta') = \frac{\pi}{\beta} \left(J_0(\kappa r) K_0(i\kappa r') + 2 \sum_1^\infty e^{i s \pi^2 / 2\beta} J_{s\pi/\beta}(\kappa r) K_{s\pi/\beta}(i\kappa r') \cos s\pi(\theta - \theta')\beta \right), \quad (11)$$

when $r < r'$; and when $r > r'$, we have to interchange r, r' in (11).

7. The physical problem can now be solved as in § 2, by associating with $u(\theta')$ of (10), the corresponding function $u(-\theta')$ for $(r', -\theta')$.

All the conditions imposed upon u, in the region

$$0 < r < \infty, \quad 0 < \theta < \beta,$$

when (r', θ') is a point in this region, are satisfied by

$$u = u(\theta') \pm u(-\theta'),$$

according as the boundary condition is $\partial u/\partial n = 0$ or $u = 0$.

Thus we have as our solution for the line-source at (r', θ') in the wedge of angle β,

$$u = \frac{i}{2\beta} \int K_0(i\kappa R) \left\{ \frac{\sin\dfrac{\pi}{\beta}a'}{\cos\dfrac{\pi}{\beta}a' - \cos\dfrac{\pi}{\beta}(\theta-\theta')} \pm \frac{\sin\dfrac{\pi}{\beta}a'}{\cos\dfrac{\pi}{\beta}a' - \cos\dfrac{\pi}{\beta}(\theta+\theta')} \right\} da',$$

(12)

the integrals being taken over the *upper* part of the path (A') of Fig. 4, or an equivalent path.

It will be seen that this agrees with Macdonald's result.*
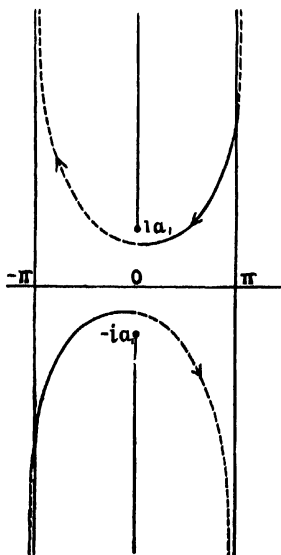
Fig. 4.—Breadth of strip, 2π; the path (A') in the a' plane.

* *Electric Waves*, p. 192.

THE EQUATION $\nabla^2 u + \kappa^2 u = 0$.

A point-source at (r', θ', z').

8. For the point-source at (r', θ', z') we start with the fundamental solution

$$u_0 = \frac{e^{-i\kappa R}}{R},$$

where $\qquad R^2 = r^2 + r'^2 + (z-z')^2 - 2rr' \cos(\theta - \theta')$.

Writing $\qquad \cosh a_1 = \dfrac{r^2 + r'^2 + (z-z')^2}{2rr'}$,

we proceed as in § 5 and transform u_0 into the integral

$$\frac{1}{2\pi} \int_R \frac{e^{ia}}{e^{-\_{-a i\theta'}}} \, da,$$

over the path (A) of Fig. 3 in the a-plane.

In this integral,

$$R = \sqrt{\{r^2 + r'^2 + (z-z')^2 - 2rr' \cos(a-\theta)\}},$$

and the remarks made above as to the cuts in the plane, the fixing of the sign of R, and the interpretation of the dotted parts of the path (A) hold as before.

Finally, the required solution of period 2β is given by

$$u = \frac{1}{2\beta} \frac{e^{-i\kappa R}}{R} \frac{e^{i\pi a/\beta}}{e^{i\pi a/\beta} - e^{i\pi\theta'/\beta}} \, da, \qquad (13)$$

over the path (A) of Fig. 3 in the a-plane.

It can be shown, as in § 6, that the expression in (13) has the following properties :—

(i) It is a solution of the differential equation.

(ii) It is periodic in θ, of period 2β.

(iii) It is everywhere finite and continuous, except at the points $(r', \theta' + 2s\beta, z')$, s being zero or any positive or negative integer. At these points it becomes infinite like $e^{-i\kappa l}/x$, when $x \to 0$.

But if the range of θ, in the space with which we are concerned, is $0 < \theta < \beta$, and if $0 < \theta' < \beta$, there will be only one infinity, and that of the proper order in this region, namely, that at (r', θ', z').

Also, if we take the solution corresponding to $-\theta'$, when $0 < \theta' < \beta$, there will be no infinity in the region $0 < \theta < \beta$ for it.

(iv) When $r \to \infty$, $u \to 0$, and there are no terms corresponding to waves reflected at infinity.

The expression in (13) can be reduced as before.

We obtain for this solution of period 2β,

$$u(\theta') = \frac{i}{2\beta} \int \frac{e^{-i\kappa R}}{R} \frac{\sin \frac{\pi}{\beta} a'}{\cos \frac{\pi}{\beta} a' - \cos \frac{\pi}{\beta} (\theta - \theta')} \, da', \qquad (14)$$

where the integral is taken over the *upper* part of the path (A') of Fig. 4 in the a'-plane, or an equivalent path, and

$$R = \sqrt{\{r^2 + r'^2 + (z - z')^2 - 2rr' \cos a'\}}.$$

9. The physical problem can now be solved as in §§ 2, 7 by associating with $u(\theta')$ of (14), the corresponding function $u(-\theta')$ for $(r', -\theta', z')$.

All the conditions imposed upon u, in the region

$$0 < r < \infty, \quad -\infty < z < \infty, \quad 0 < \theta < \beta,$$

when (r', θ', z') is a point in this region, are satisfied by

$$u = u(\theta') \pm u(-\theta'),$$

according as the boundary condition is $\partial u / \partial n = 0$ or $u = 0$.

Thus we have as our solution for the point-source at (r', θ', z') in the wedge of angle β,

$$u = \frac{i}{2\beta} \int \frac{e^{-i\kappa R}}{R} \left\{ \frac{\sin \frac{\pi}{\beta} a'}{\cos \frac{\pi}{\beta} a' - \cos \frac{\pi}{\beta} (\theta - \theta')} \pm \frac{\sin \frac{\pi}{\beta} a'}{\cos \frac{\pi}{\beta} a' - \cos \frac{\pi}{\beta} (\theta + \theta')} \right\} da',$$

$$(15)$$

the integral being taken over the *upper* part of the path (A') of Fig. 4 in the a'-plane, or an equivalent path.

This agrees with Macdonald's solution.[*]

10. *Oblique incidence of plane waves on a wedge of angle β.*[†]

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[*] *Loc. cit., Proc. London Math. Soc.*, Ser. 2, Vol. 14 (1915), p. 421.

It will be noticed that I have made some changes in the diagram which correspond to Fig. 6 of my previous paper (M.S.).

[†] For oblique incidence on the semi-infinite plane ($\beta = 2\pi$), cf. *Proc. Edinburgh Math. Soc.*, Vol. 19 (1901), p. 71.

The edge of the wedge is supposed not to be perpendicular to the direction of the waves. Spherical polar coordinates (r, θ, ϕ) are used, the origin being in the edge of the wedge, and this line is taken as the initial line for the angle θ or the axis of z.

The space with which we are concerned in the physical problem is given by

$$0 < r < \infty, \quad 0 < \theta < \pi, \quad 0 < \phi < \beta,$$

the plane surfaces of the wedge being $\phi = 0$ and $\phi = \beta$.

We suppose that the line (l, m, n), defined by (θ', ϕ') (Fig. 5) is perpendicular to the front of the waves.
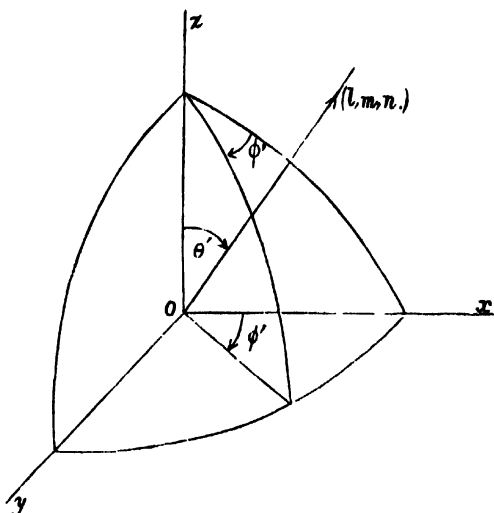
Fig. 5.

The fundamental solution in this case is

$$u_0 = e^{i\kappa(lx + my + nz)} = e^{i\kappa[\cos\theta\cos\theta' + \sin\theta\sin\theta'\cos(\phi - \phi')]}.$$

We transform this as in § 1 into the integral

$$\frac{e^{i\kappa r\cos\theta\cos\theta'}}{2\pi} \int e^{i\kappa r\sin\theta\sin\theta'\cos(\alpha - \phi)} \frac{e^{i\alpha}}{e^{i\alpha} - e^{i\phi}} \, d\alpha,$$

over the path (A) of Fig. 1; the only change necessary in this figure is to insert ϕ in place of θ.

We are then brought to the solution of period 2β in ϕ,

$$u = \frac{e^{i\kappa r \cos\theta \cos\theta'}}{2\beta} \int e^{i\kappa r \sin\theta \sin\theta' \cos(a-\phi)} \frac{e^{i\pi a/\beta}}{e^{i\pi a/\beta} - e^{i\pi\phi'/\beta}} \, da, \qquad (16)$$

over the path (A) of Fig. 1 in the a-plane.

This expression has the following properties :—

   (i) It is a solution of the differential equation.

   (ii) It is periodic in ϕ, of period 2β.

   (iii) It is finite and continuous.

   (iv) When $r \to \infty$, it takes the value $\sum e^{i\kappa r (\cos\theta \cos\theta' + \sin\theta \sin\theta' \cos(\phi-\phi'-2s\beta))}$, the summation extending to the angles $\phi' + 2s\beta$ which lie within $\pm \pi + \phi$, s being zero or any positive or negative integer.

The expression in (16) is reduced, as before, to

$$u(\phi') = \frac{i e^{i\kappa r \cos\theta \cos\theta'}}{2\beta} \int e^{i\kappa r \sin\theta \sin\theta' \cos a'} \frac{\sin\frac{\pi}{\beta} a'}{\cos\frac{\pi}{\beta} a' - \cos\frac{\pi}{\beta}(\phi-\phi')} \, da', \quad (17)$$

over the *upper* part of the path (A') of Fig. 2 in the a'-plane, or an equivalent path.

Also it is not difficult to show that this function $u(\phi')$ satisfies the equation

$$u(\phi') = \frac{\pi}{\beta} e^{i\kappa r \cos\theta \cos\theta'}$$

$$\times \left\{ J_0(\kappa r \sin\theta \sin\theta') + 2 \sum_1^\infty e^{i s \pi^2/2\beta} J_{s\pi/\beta}(\kappa r \sin\theta \sin\theta') \cos s\pi(\phi-\phi')/\beta \right\} . \quad (18)$$

11. For the physical problem, the solution is given as in §§ 2, 7, and 9, by

$$u = u(\phi') \pm u(-\phi'),$$

according as the boundary condition is $\partial u/\partial n = 0$ or $u = 0$.

Thus we have

$$u = \frac{i}{2\beta} e^{i\kappa r \cos\theta \cos\theta'} \int e^{i\kappa r \sin\theta \sin\theta' \cos a}$$

$$\times \left\{ \frac{\sin\frac{\pi}{\beta} a'}{\cos\frac{\pi}{\beta} a' - \cos\frac{\pi}{\beta}(\phi-\phi')} \pm \frac{\sin\frac{\pi}{\beta} a'}{\cos\frac{\pi}{\beta} a' - \cos\frac{\pi}{\beta}(\phi+\phi')} \right\} \, da', \quad (19)$$

over the *upper* part of the path (A′) of Fig. 2 in the α'-plane, or an equivalent path.

And in series, using cylindrical coordinates (ϖ, ϕ, z), we have

$$u = \frac{2\pi}{\beta} e^{i\kappa z \cos \theta'}$$

$$\times \left\{ J_0(\kappa\varpi \sin \theta') + 2 \sum_1^\infty e^{i s \pi^2/2\beta} J_{s\pi/\beta}(\kappa\varpi \sin \theta') \cos s\pi\phi/\beta \cos s\pi\phi'/\beta \right\} \quad (20)$$

or

$$u = \frac{4\pi}{\beta} e^{i\kappa z \cos \theta'} \sum^\alpha e^{i s \pi^2/2\beta} J_{s\pi/\beta}(\kappa\varpi \sin \theta') \sin s\pi\phi/\beta \sin s\pi\phi'/\beta$$

The results in §§ 10 and 11 can be deduced from the solution for the point-source at (r', θ', ϕ'), by taking as fundamental solution*

$$\frac{r'}{R} e^{-i\kappa R},$$

and then letting $r' \to \infty$.

* Cf. Bromwich, *loc. cit.*, p. 461.

Bromwich's Method of solving Problems in the Conduction of Heat. By Prof. H. S. CARSLAW, Sc.D.

1. IN his paper—" Examples of Operational Methods in Mathematical Physics," Philosophical Magazine, No. 220, April 1919—Bromwich advocates the use of so-called operational methods, following Heaviside, in electrical and other physical problems, and illustrates his method by the solution of various questions, including some in the Conduction of Heat. In an earlier paper (Proc. London Math. Soc. (Ser. 2) xv. p. 401, 1917) he discussed Heaviside's work, and confirmed it by the aid of contour integrals.

The object of the present paper is to illustrate by some

problems in linear flow the method which Bromwich's work has led me to adopt in the discussion of a large class of problems in the Conduction of Heat. It seems to me easier to build up the required solution by integrating a suitable solution over a certain standard path in the plane of the complex variable. The proper particular solution will be easily obtained after a little practice in the method.

The problems in §§ 2, 3, and 4 have been chosen for their simplicity. They are, of course, elementary and solvable by the ordinary methods. The problem in § 5 is here solved for the first time. The corresponding cases for the semi-infinite rod, and the sphere composed of two different materials, can be treated in the same way. These two questions are referred to by Heaviside * in his discussion of the Age of the Earth, following upon Perry's criticism † of Kelvin's classical treatment of this subject.

2. *Rod of length a.   The ends $x=0$ and $x=a$ kept at temperatures zero and v_0 respectively.   The initial temperature zero.*

Let the temperature at the point x at the time t be v.
Then the equations are as follows :—

$$\frac{\partial v}{\partial t} = \kappa \frac{\partial^2 v}{\partial x^2}, \quad 0 < x < a. \quad . \quad . \quad . \quad (1)$$

$$v = 0, \quad \text{when } x = 0. \quad . \quad . \quad . \quad . \quad (2)$$

$$v = v_0, \quad \text{when } x = a. \quad . \quad . \quad . \quad . \quad (3)$$

$$v = 0, \quad \text{when } t = 0. \quad . \quad . \quad . \quad . \quad (4)$$

Fig. 1.

- ∞   o   +∞
The path (P) in the α-plane.

Consider the value of v given by the integral

$$v = \frac{v_0}{i\pi} \int \frac{\sin \alpha x \ e^{-\kappa \alpha^2 t}}{\sin \alpha a \ \alpha} d\alpha \quad . \quad . \quad . \quad . \quad (5)$$

over the path (P) of fig. 1 in the α-plane.   In this path the

* Heaviside, 'Electromagnetic Theory,' Vol. II. Chapter v. *Cf.* §§ 229, 230.
† 'Nature,' h. p. 224 *et seq.* (18 5).

argument of α on the right must lie between 0 and $\frac{1}{4}\pi$, and on the left between $\frac{3}{4}\pi$ and π. We take the path (P) of fig 1 as the standard path in the problems which follow.

Since every element of the integral satisfies (1), the value of v in (5) satisfies (1).

Also when $x=0$, we have $v=0$.

And when $x=a$, $v=\dfrac{v_0}{i\pi}\displaystyle\int_{}^{}\dfrac{e^{-\kappa\alpha^2 t}}{\alpha}\,d\alpha$, over the path (P). (6)

Since the integrand is an odd function of α, if we form the path (Q) by taking the image of the path (P) in the real

Fig. 2.
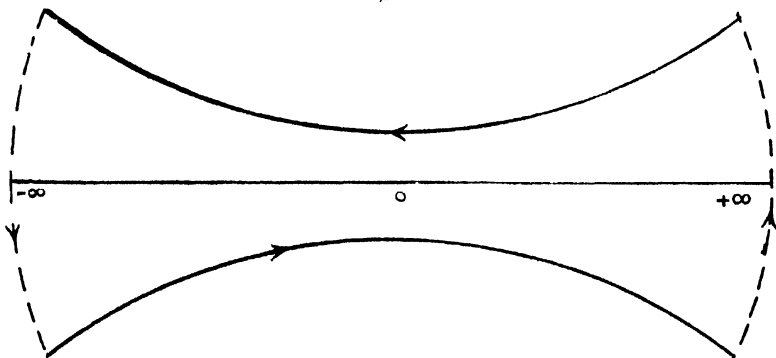
The path (Q) in the α-plane.

axis of α, joining the ends of the path (P) and its image by arcs of a circle, centre at the origin, whose radius tends to infinity, we have from (6)

$$= \frac{v_0}{2i\pi}\int_{}^{}\frac{{}^{\alpha^2 t}}{}\,d\alpha, \quad \text{over the path (Q),}$$

since the integrals over the circular arcs vanish in the limit.

Therefore when $x=a$, we have $v=v_0$.

Finally, when $t=0$, we have

$$v=\frac{v_0}{i\pi}\int\frac{\sin \alpha x\,d\alpha}{\sin \alpha a\ \ \alpha}, \quad \text{over the path (P).}$$

Now the integrand has no infinities above the path (P), and if we complete the circuit by the arc of a circle, dotted in fig. 3, whose centre lies at the origin and radius tends to infinity, the integral over the complete path of fig. 3 is zero.

But the integral over the dotted path vanishes in the limit. Therefore $v=0$, when $t=0$.

It follows that the value of v given by (5) satisfies all the conditions of our problem.

Fig. 3.
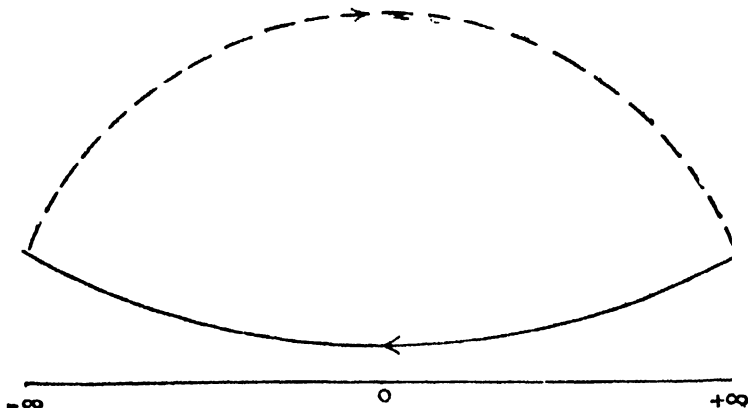
The solution obtained in (5) as a contour integral is transformed into an infinite series by Cauchy's Theorem, using the path (Q) of fig. 2.

For we have

$$v = \frac{v_0}{2i\pi} \int \frac{\sin \alpha x}{\sin \alpha a} \frac{e^{-\kappa a^2 t}}{\alpha} d\alpha, \quad \text{over the path (Q)},$$

$$= v_0 \left[\frac{x}{a} + \frac{2}{\pi} \sum_1^\infty \frac{(-1)^n}{n} \sin \frac{n\pi}{a} x\, e^{-\kappa \frac{n^2\pi^2}{a^2} t} \right].$$

3. *The same rod. The end $x=0$ kept at zero; radiation into a medium at v_0 at the end $x=a$. The initial temperature zero.*
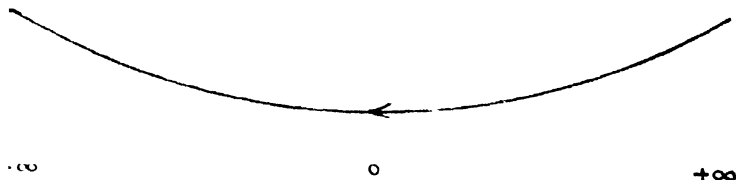
Here we have to solve :—

$$\frac{\partial v}{\partial t} = \kappa \frac{\partial^2 v}{\partial x^2}, \quad 0 < x < a. \quad \cdots \cdots (1)$$

$$v = 0, \quad \text{when } x=0. \quad \cdots \cdots (2)$$

$$\frac{\partial v}{\partial x} + h(v - v_0) = 0, \quad \text{when } x=a. \quad \cdots (3)$$

$$v = 0, \quad \text{when } t=0. \quad \cdots \cdots (4)$$

Starting from the solution of (1)

$$A \sin \alpha x \, e^{-\kappa \alpha^2 t}$$

which vanishes at $x = 0$, we are led by (3) to choose A so that

$$\alpha A \cos \alpha a + h(A \sin \alpha a - r_0) = 0 \; ;$$

i. e.
$$A = \frac{h r_0}{\alpha \cos \alpha a + h \sin \alpha a}.$$

This brings us to the solution of our problem in the form

$$v = \frac{h r_0}{i \pi} \int \frac{\sin \alpha x}{\alpha \cos \alpha a + h \sin \alpha a} \, \frac{e^{-\kappa \alpha^2 t}}{\alpha} \, d\alpha, \quad \text{over the path (P). (5)}$$

It can be shown just as in § 2 that the value of v given in (5) as a contour integral satisfies all the conditions of the problem, for the roots of the equation

$$\alpha \cos \alpha a + h \sin \alpha a = 0 \quad . \quad . \quad . \quad . \quad (6)$$

are all real *, and in the integral

$$\int \frac{\sin \alpha x}{\alpha \cos \alpha a + h \sin \alpha a} \, \frac{d\alpha}{\alpha}$$

the path (P) can be replaced by the dotted part of fig. 3, so that, when the radius tends to infinity, this integral vanishes.

Finally the solution obtained in (5) reduces as in § 2, by Cauchy's Theorem, to a infinite series, and we have

$$v = h r_0 \left[\frac{x}{1 + ha} + 2 \sum_1^\infty \frac{(-1)^n \sqrt{(\alpha_n^2 + h^2)}}{(h(1 + ha) + a \alpha_n^2)} \, \frac{\sin \alpha_n x}{\alpha_n} \, e^{-\kappa \alpha_n^2 t} \right],$$

the summation being taken over the positive roots of (6).

4. If the end $x = a$ is kept at temperature Ct, or radiation takes place there into a medium at temperature Ct, the solutions corresponding to § 2 (5) and § 3 (5) will be seen to be

$$v = -\frac{C}{\kappa i \pi} \int \frac{\sin \alpha x}{\sin \alpha a} \, \frac{e^{-\kappa \alpha^2 t}}{\alpha^3} \, d\alpha,$$

$$v = -\frac{Ch}{\kappa i \pi} \int \frac{\sin \alpha x}{\alpha \cos \alpha a + h \sin \alpha a} \, \frac{e^{-\kappa \alpha^2}}{\alpha^3} \, d\alpha,$$

respectively, the integrals being taken over the standard path (P).

These can be reduced to infinite series as before, by introducing the path (Q).

* *Cf.* Carslaw, 'Fourier's Series and Integrals,' § 133.

5. *Rod of length b composed of two different materials. The ends $x=0$ and $x=b$ kept at zero and v_0 respectively. The initial temperature zero.*

Let v_1 be the temperature in the first part of the rod $(0 < x < a)$, and K_1, c_1, ρ_1 be its conductivity, specific heat, and density. Let v_2 be the temperature in the other part $(a < x < b)$, and K_2, c_2, ρ_2 the corresponding constants therein. Also let

$$\kappa_1 = K_1/c_1\rho_1 \quad \text{and} \quad \kappa_2 = K_2/c_2\rho_2.$$

The equations for the temperature are as follows:—

(1) $\dfrac{\partial v_1}{\partial t} = \kappa_1 \dfrac{\partial^2 v_1}{\partial x^2}$, $0 < x < a$: $\dfrac{\partial v_2}{\partial t} = \kappa_2 \dfrac{\partial^2 v_2}{\partial x^2}$, $a < x < b$. (1')

(2) $v_1 = 0$, when $x = 0$: $v_2 = v_0$, when $x = b$.   (2')

(3) $v_1 = 0$, when $t = 0$: $v_2 = 0$, when $t = 0$.   (3')

$$v_1 = v_2, \quad \text{when } x = a. \quad . \quad . \quad . \quad . \quad (4)$$

$$K_1 \frac{\partial v_1}{\partial x} = K_2 \frac{\partial v_2}{\partial x}, \quad \text{when } x = a. \quad . \quad . \quad . \quad (5)$$

It is clear that

$$v_1 = A_1 \sin \alpha x\, e^{-\kappa_1 \alpha^2 t},$$

and $v_2 = (A_2 \sin \mu\alpha(x-a) + B_2 \sin \mu\alpha(b-x))\,e^{-\kappa_1 \alpha^2 t}$,

satisfy (1) and (1'), when $\mu = \sqrt{(\kappa_1/\kappa_2)}$.
They also satisfy (4) and (5), provided that

$$A_1 \sin \alpha a = B_2 \sin \mu\alpha(b-a),$$

and $K_1 A_1 \cos \alpha a = K_2 \mu(A_2 - B_2 \cos \mu\alpha(b-a))$.

Therefore we take

$$A_2 = (\sigma \cos \alpha a + \sin \alpha a \cot \mu\alpha(b-a)) A_1,$$

and $B_2 = \dfrac{\sin \alpha a}{\sin \mu\alpha(b-a)} A_1$,

where $\sigma = \dfrac{K_1}{K_2 \mu} = \sqrt{\left(\dfrac{K_1 c_1 \rho_1}{K_2 c_2 \rho_2}\right)}$.

Introducing the path (P) and choosing a suitable value for A_1, we are led to the solution:—

$$v_1 = \frac{v_0}{i\pi} \int \frac{\sin \alpha x}{F(\alpha)} \frac{e^{-\kappa_1 \alpha^2 t}}{\alpha}\, d\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$v_2 = \frac{i\pi}{v_0} \int \left(\frac{\sin \mu\alpha(x-a)}{\sin \mu\alpha(b-a)} + \frac{\sin \alpha a \sin \mu\alpha(b-x)}{F(\alpha) \sin \mu\alpha(b-a)}\right) \frac{e^{-\kappa_1 \alpha^2 t}}{\alpha}\, d\alpha, \quad (7)$$

where

$$F(\alpha) = \sigma \cos \alpha a \sin \mu\alpha(b-a) + \sin \alpha a \cos \mu\alpha(b-a),$$

and these integrals are taken over the standard path (P).

The second integral reduces to

$$v_2 = \frac{v_0}{i\pi} \int \frac{\sigma \cos \alpha a \sin \mu\alpha(x-a) + \sin \alpha a \cos \mu\alpha(x-a)}{\sigma \cos \alpha a \sin \mu\alpha(b-a) + \sin \alpha a \cos \mu\alpha(b-a)} \frac{e^{-\kappa_1\alpha^2 t}}{\alpha} d\alpha$$

over the path (P).   . . . (8)

The values v_1 and v_2 given in (6) and (8) satisfy all the conditions of our problem : for, from the way in which they have been built up, they obviously satisfy the differential equations (1) and (1′), and (2), (4), and (5).

Further, putting $x = b$ in (8), we have $v = v_0$.

We shall prove below that the roots of the equation

$$F(\alpha) \equiv \sigma \cos \alpha a \sin \mu\alpha(b-a) + \sin \alpha a \cos \mu\alpha(b-a) = 0 \quad (9)$$

are infinite in number, all real and not repeated, and it is clear that to each positive root there corresponds an equal and opposite negative root.

Assuming this to be the case, the same argument as in § 2 will show that the initial conditions (3) and (3′) are satisfied.

Finally, the solution is obtained as an infinite series. For we have, from (6) and (8),

$$v_1 = \frac{v_0}{2i\pi} \int \frac{\sin \alpha x}{F(\alpha)} \frac{e^{-\kappa_1\alpha^2 t}}{\alpha} d\alpha,$$

$$v_2 = \frac{v_0}{2i\pi} \int \frac{\sigma \cos \alpha a \sin \mu\alpha(x-a) + \sin \alpha a \cos \mu\alpha(x-a)}{F(\alpha)} \frac{e^{-\kappa_1\alpha^2 t}}{\alpha} d\alpha,$$

over the path (Q) of fig. 2.

Therefore

$$v_1 = \frac{v_0 x}{\sigma\mu(b-a) + a} + 2v_0 \sum_1^\infty \frac{\sin \alpha_n x \; e^{-\kappa_1\alpha_n^2 t}}{F'(\alpha_n) \; \alpha_n},$$

$$v_2 = v_0 \frac{\sigma\mu(x-a) + a}{\sigma\mu(b-a) + a}$$

$$+ 2v_0 \sum_1^\infty \frac{\sigma \cos \alpha_n a \sin \mu\alpha_n(x-a) + \sin \alpha_n a \cos \mu\alpha_n(x-a)}{F'(\alpha_n)} \frac{e^{-\kappa_1\alpha_n^2 t}}{\alpha_n},$$

the summation being taken over the positive roots of (9).

6. It remains to discuss the roots of the equation

$$F(\alpha) \equiv \sigma \cos \alpha a \sin \mu\alpha(b-a) + \sin \alpha a \cos \mu\alpha(b-a) = 0.$$

From the graphs of

$$y = \sigma \cot \alpha a$$

and　　　　$$y = -\cot \mu\alpha(b-a)$$

it is clear that there are infinite number of real roots, and the position of the same can be determined.

Also $F(\alpha)$ is an odd function of α and the real roots may be denoted by

$$0, \quad \pm \alpha_1, \quad \pm \alpha_2, \quad \ldots.$$

By examining $F'(\alpha)$, it will be seen that these roots are not repeated.

Also it is clear that $F(\alpha)$ has no pure imaginary root. We have now to show that it has no roots of the form $\xi \pm i\eta$.

Consider the functions U_1, U_2 defined as follows:—

$$U_1 = \sin \alpha x, \quad 0 < x < a$$

$$U_2 = \frac{\sin \mu\alpha(b-x)}{\sin \mu\alpha(b-a)} \sin \alpha a, \quad a < x < b,$$

where α is a root of $F(\alpha) = 0$,

and　　　$\sigma = K_1/K_2\mu, \qquad \mu = \sqrt{(\kappa_1/\kappa_2)}.$

Then we have

$$\frac{d^2U_1}{dx^2} + \alpha^2 U_1 = 0, \qquad 0 < x < a ; \quad \ldots \quad (1)$$

$$\frac{d^2U_2}{dx^2} + \mu^2\alpha^2 U_2 = 0, \qquad 0 < x < b. \quad \ldots \quad (2)$$

Also　　　$U_1 = 0,$　when $x = 0.$ $\ldots \ldots \ldots$ (3)

$$U_1 = U_2 \\ K_1 \frac{dU_1}{dx} = K_2 \frac{dU_2}{dx} \Bigg\} \text{ when } x = a. \quad \ldots \ldots \quad (4)$$

And　　　$U_2 = 0,$　when $x = b.$ $\ldots \ldots \ldots$ (5)

Let β be another root of $F(\alpha) = 0$, and V_1, V_2 the corresponding functions.

Then we have, from (1) and (2),

$$\frac{\mu}{\sigma}(a^2-\beta^2)\int_a^b U_2V_2 dx + \frac{1}{\sigma\mu}\int_a^b (V_2U_2'' - U_2V_2'')dx = 0,$$

and

$$(a^2-\beta^2)\int_0^a U_1V_1 dx + \int_0^a (V_1U_1'' - U_1V_1'')dx = 0.$$

Therefore

$$(a^2-\beta^2)\left[\int_0^a U_1V_1 dx + \frac{\mu}{\sigma}\int_a^b U_2V_2 dx\right]$$

$$= \int_0^a (U_1V_1'' - V_1U_1'')dx + \frac{1}{\sigma\mu}\int_a^b (U_2V_2'' - V_2U_2'')dx$$

$$= \left[U_1V_1' - V_1U_1'\right]_0^a + \frac{K_2}{K_1}\left[U_2V_2' - V_2U_2'\right]_a^b.$$

It follows from (3), (4), and (5), that

$$(a^2-\beta^2)\left[\int_0^a U_1V_1 dx + \frac{\mu}{\sigma}\int_a^b U_2V_2 dx\right] = 0.$$

Thus $F(a)=0$ cannot have imaginary roots of the form $\xi \pm \iota\eta$.

A NOTE ON A RELATION BETWEEN THE THERMAL CONDUCTIVITY AND THE VISCOSITY OF GASES.

By J. A. POLLOCK, F.R.S.

THERMAL CONDUCTIVITY AND VISCOSITY

OF GASES.

A NOTE ON A RELATION BETWEEN THE THERMAL CONDUCTIVITY AND THE VISCOSITY OF GASES.

By J. A. POLLOCK, F.R.S.

IN a recent number of the Proceedings of the Royal Society of London, Hercus and Laby[1] publish the details of an accurate redetermination of the thermal conductivity of air. Combining their result with those of eleven other experimenters, they give as the most probable value of the conductivity at $0°$ C., $k = 5\cdot22 \times 10^{-5}$.

In 1913 Eucken[2] gave the results of a series of measurements of the thermal conductivities of a number of gases relative to that of air, the determinations being reduced to absolute measure by considering the conductivity of air as $5\cdot66 \times 10^{-5}$. As shown by Hercus and Laby, the new determination of this latter constant is at once useful, as it enables Eucken's absolute values to be put on a more accurate basis.

After reviewing the whole evidence, Hercus and Laby have collected for the various gases the most probable values of the following constants:—k, the thermal conductivity, C_p, the specific heat at constant pressure, γ, the ratio of the specific heats, and η, the viscosity, and with these results have calculated the values of f given by the equation,

$$f = \frac{\gamma\, k_0}{\eta_0\, C_p} \qquad \dots\dots\dots\dots\dots\dots\dots (1)$$

As the value of f depends on the atomicity of the molecule, attempts have been made to find a relation between f and γ. Jeans[3] has suggested the formula, $f = (9\gamma - 5)/4$.

[1] Hercus and Laby, Proc. Roy. Soc., A, 95, p. 190, 1919.

[2] Eucken, Phys. Zeit., 14, p. 324, 1913.

[3] Jeans, The Dynamical Theory of Gases, 2nd ed., p. 317, 1916.

The values calculated by this equation agree very well with the values obtained from equation (1) if Eucken's original results for the conductivities are used. When, however, the conductivity of air is taken as 5.22×10^{-5} instead of 5.66×10^{-5}, the expression is no longer accurate, and Hercus and Laby suggest, on empirical grounds, another linear form,

$$f = 2.816\, \gamma - 2.2 \dotfill (2)$$

which gives numbers closely agreeing, in the majority of cases, with the results they obtain from equation (1).

I had previously mentioned[1] that the values of f, calculated by equation (1) with Eucken's original numbers for the conductivities, are approximately represented by an equation of the form, $f = a\,(\gamma-1)/\gamma$, where a is a constant. I have now found a value of a appropriate to the new values of f, and the expression becomes

$$f = \frac{6.15\,(\gamma - 1)}{\gamma} \dotfill (3)$$

In Table I the values of f obtained from equations (2) and (3) are compared with those given by the defining equation (1). An inspection of the differences, $1-2$ and $1-3$ in the fifth and sixth columns of the table, shows, that although the differences $1-3$ are on the whole smaller, there is little to choose between the two expressions, but equation (3) has an advantage in that it indicates for perfect gases a simple approximate relation between the conductivity and the viscosity which may be put in the form

$$\frac{m\,\gamma\,k_o}{\eta_o} = 2a$$

where m is the molecular mass and a the constant of equation (3). How this relation fares in the case of actual gases may be seen by an inspection of the calculated values of $2a$ given in the last column of the table.

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[1] Pollock, Jour. and Proc., Roy Soc. N.S.W., XLIX, p. 249, 1915. I now learn that Hercus and Laby's paper was set down to be read before the meeting of the British Association in Australia in 1914, but owing to pressure of other business was not reached. The paper was, therefore, completed for publication before my previous note was written.

Table 1.

Gas.	f $\dfrac{\gamma k_o}{\eta_o C_p}$ 1	f (empirical) $2 \cdot 816\gamma - 2 \cdot 2$ 2	$\dfrac{6 \cdot 15\,(\gamma - 1)}{\gamma}$ 3	Differences. $1 - 2$	$1 - 3$	$\dfrac{m\gamma k_o}{\eta_o}$
He	2·31	2·49	2·46	− ·18	− ·15	11·6
A	2·47	2·49	2·46	− ·02	+ ·01	12·2
Ne	...	2·42	2·40	...	...	12·0
H₂	1·76	1·74	1·75	+ ·02	+ ·01	11·9
N₂	1·76	1·75	1·76	+ ·01	·00	12·1
O₂	1·79	1·75	1·76	+ ·04	+ ·03	12·5
Air	1·76	1·75	1·76	+ ·01	·00	12·3
NO	1·73	1·73	1·75	·00	− ·02	11·9
CO	1·72	1·76	1·77	− ·04	− ·05	11·8
Cl₂	1·50	1·58	1·56	− ·08	− ·06	12·8
CO₂	1·45	1·46	1·42	− ·01	+ ·03	13·0
N₂O	1·47	1·51	1·48	− ·04	− ·01	14·2
H₂S	1·34	1·51	1·48	− ·17	− ·14	10·9
SO₂	1·35	1·34	1·26	+ ·01	+ ·09	12·0
CS₂	1·25	1·29	1·18	− ·04	+ ·07	15·2
NH₃	1·23	1·48	1·44	− ·25	− ·21	11·0
C₂H₂	...	1·35	1·27	...	...	14·1
CH₄	1·45	1·51	1·48	− ·06	− ·03	13·7
C₂H₄	1·27	1·32	1·23	− ·05	+ ·04	14·3
C₂H₆	...	1·24	1·11	...	...	16·8

In Table II. I give the values of $m\,k_o/\eta_o$.

Table II.

Gas.	$\dfrac{mk_o}{\eta_o}$	Gas.	$\dfrac{mk_o}{\eta_o}$
He	6·95	CO₂	10·02
A	7·31	N₂O	10·78
Ne	7·29	H₂S	8·28
		SO₂	9·57
H₂	8·52	CS₂	12·25
N₂	8·60		
O₂	8·89	NH₃	8·44
Air	8·74	C₂H₂	11·19
NO	8·52	CH₄	10·44
CO	8·43	C₂H₄	11·44
Cl₂	9·55	C₂H₆	13·79

In Table III the values of the constants are given which have been used in the calculation of the results shown in Tables I and II. These values have been copied from Hercus and Laby's paper with the exception of a few additional entries which have been made from sources mentioned in the footnotes.

Table III.

Gas.	m	$k_0 \times 10^5$		C_p		γ		$\eta_0 \times 10^4$	
He	4	32·7	2(a)	1·255	2	1·667 (b)		1·883	5
A	40	3·85	2	0·123	1	1·667	1	2·108	3
Ne	20	10·87 (c)		...		1·642 (f)		2·981 (e)	
H$_2$	2	36·3	9	3·407	5	1·399	4	0·852	12
N$_2$	28	5·14	3	0·241	4	1·401	3	1·673	5
O$_2$	32	5·35	4	0 218	4	1·401	4	1·925	6
Air	29	5·22	14	0 239	7	1·402	18	1·733	31
NO	30	4·93	2	0·231	1	1·397	1	1·737	2
CO	28	5·05	3	0·246	2	1·405	2	1 677	3
Cl$_2$	71	1·69	1	0·120	2	1·341	3	1·256	2
CO$_2$	44	3·25	10	0·2015	6	1·300	13	1·428	12
N$_2$O	44	3·34	3	0·220	2	1·317	2	1·364	3
H$_2$S	34	2·81	1	0 2389	3	1·317	3	1·154	1
SO$_2$	64	1·80	1	0·1527	2	1·258	3	1·204	2
CS	76	1·49 (d)		0·160 (f)		1·239 (f)		0·924 (d)	
NH$_3$	17	4·71	3	0·531	2	1·306	3	0·949	3
C$_2$H$_2$	26	4·06 (d)		...		1·26 (f)		0 943 (d)	
CH$_4$	16	6·76	3	0·592	2	1·316	3	1·036	2
C$_2$H$_4$	28	3·84	3	0·404	2	1·250	4	0·940	4
C$_2$H$_6$	30	3·93 (d)		...		1·22 (f)		0·855 (d)	

"(a) The number given after each constant is the number of values of which it is the mean. (b) The theoretical value is used in preference to the one observed value 1·63 of Behn and Geiger." (c) Weber, see Sci. Abs. 313, 1919. (d) Eucken, loc. cit. (e) Rankine, Phil. Mag. 21, p. 45, 1911. (f) Kaye and Laby's Tables, 2nd ed. All other values from Hercus and Laby, loc. cit.

DETERMINATIONS OF HEAT CONDUCTIVITY
OF SELENIUM.

SOME DETERMINATIONS OF THE HEAT CONDUC-
TIVITY OF SELENIUM.

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(Communicated by Professor O. U. VONWILLER.)

IT is well known that the electrical conductivity of selenium can be varied over a wide range by suitable alter-ations in the method of preparation, or in the temperature and degree of illumination at the time of testing. If these changes are due to variations in the number of free elec-trons present in the substance, we should expect to find corresponding changes in the thermal conductivity under similar conditions.

Some investigations on this point have been made by Bellati and Lussana,[1] and by L. P. Sieg.[2] In both cases attention was concentrated mainly on the effect of illumin-ation, and only relative measurements were made. In the work which is to be described here, the influence of the method of preparation, the age of the specimen, and the temperature of testing have been investigated, all measure-ments being made with the selenium in darkness.

The results obtained are such as might be expected from a consideration of the values of the electrical conductivity obtained by observers working with selenium cells. It is found that the thermal conductivity varies over a wide range, being affected by those conditions which influence the electrical conductivity. In all the cases which have been examined, both thermal and electrical conductivities

[1] Gazz. Chim. Ital., 17, 391.   [2] Phys. Rev., 6, p. 213, 1915.

are changed in a similar manner, but the relative alteration produced in the former is, in general, smaller than that brought about in the latter property by the same cause.

Although the values of the conductivity have been obtained throughout in absolute units, very little weight should be attached to the actual figures given for the crystalline form. For it appears probable that in any preparation of crystalline selenium, spontaneous changes take place for a long time after preparation, and, in addition, the slight alteration of temperature which is necessary before any measurement can be made, is able, under certain conditions, to produce a considerable change in the conductivity.

The results may be summarized briefly as follows:—

(1) The thermal conductivity of vitreous selenium at 25° C. was found to lie between 0·000293 and 0·000328.

(2) The conductivity of crystalline selenium at 25° C. varied from 0·00070 to 0·00183. In general the conductivity increased with the temperature of preparation, but diminished with age.

(3) In all the cases examined, the temperature coefficient was positive.

Method of Investigation.

The method used was that described by C. H. Lees.[1] The selenium was tested in the form of a disc 6·5 cm. in diameter, and of the order of 0·5 cm. in thickness. All temperatures were measured by means of copper-eureka thermo-couples which were carefully calibrated at the commencement of the work. A year later other similar thermo-couples were substituted, and new calibration readings taken. The series method of measuring thermo-electromotive-forces employed by Lees was not used. Each

[1] Phil. Trans., A, 1898, p. 399.

e.m.f. was measured independently by means of a Wolff potentiometer, and the temperature calculated from tables prepared from the calibration readings. The only other alteration in the method was the substitution of a Weston milliammeter and voltmeter for the wattmeter which Lees used to measure the rate at which heat was supplied.

The discs were first prepared in the vitreous[1] form by pouring molten selenium into a hot iron mould. These were transformed to the crystalline state by heating in an oil oven to some chosen temperature. They were then ground with fine emery and polished.

On account of the contraction which takes place when changing from the vitreous to the crystalline form, some difficulty was experienced owing to discs cracking during heating. This was overcome by performing all operations very slowly. The vitreous discs were gradually cooled from the molten state, and the oven was so regulated that the required temperature was only reached after seven hours continuous heating. This temperature was maintained for one hour, and the disc was allowed to cool slowly in the oven. By this means crystalline discs were prepared at temperatures which range from 160° C. to 214° C. Some specimens were also tested in the vitreous form.

If the bath in which the discs were tested were heated by a suitable current in the bath heating coil, the conductivity could be measured at any temperature higher than that of the room. An upper limit is, however, placed on the temperature of testing by the fact that selenium is so readily changed by heating even to comparatively low temperatures. Thus the available range was only about 25° C. to 55° C. In order to obtain sufficiently steady temperature conditions, it was found necessary to keep the current in the heating coil constant for approximately six

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[1] A. P. Saunders, Jour. Phys. Chem., Vol. IV, p. 423, 1900.

hours before any reading could be taken. When this steady temperature was reached, two sets of readings were taken, separated by an interval of half an hour. Thus in Table 1 we have, at every temperature, two values of the conductivity, each of these being calculated from the mean of a number of readings.

Table I also shows the general order adopted for any disc. The conductivity was measured first at room temperature, then at several higher temperatures, and finally the readings at room temperature were repeated. In most cases this procedure has been repeated at intervals which extend up to one year from the date of preparation.

Sources of Error.

The errors involved were necessarily large. They naturally fall into two divisions, those due to the imperfections of apparatus and method, and those due to such changes in the selenium as were beyond control.

With the instruments used, the errors of the first class should not have exceeded 1%, these probably being small in comparison with the errors of the second class.

The latter appear to be due chiefly to heating effects, and are most marked in the case of newly prepared crystalline discs. Two types of irregularity were of frequent occurrence:—

(i.) In many cases the first reading taken for any crystalline disc at a temperature above that of the room was abnormally high.

(ii.) The conductivity at room temperature was almost invariably increased after the measurements at higher temperatures had been made, but the actual increase thus produced varied greatly, even in the case of discs which had apparently been treated in exactly the same manner.

Results.

Eleven discs have been prepared, five vitreous and six crystalline, the nature of the results obtained being illustrated in Tables I, II and V.

Table I.—*Conductivity of Vitreous Selenium.*
Disc 2, prepared on 21 August, 1916.
Thickness of disc = 0·7523 c.m.

Read-ing.	Date.	Temperature of disc.	Temperature gradient across disc.	Heat supplied (calories per sec.)	Thermal Conductivity.
(i)	22 Aug., 1916	23·80 C.	5·39	0·1724	0·000324
(ii)		23·92	5·46	0·1724	0 000319
(iii)	23 Aug., 1916	33·69	4·93	0·1651	0·000345
(iv)		35·94	4·98	0·1650	0·000342
(v)	24 Aug., 1916	40·92	4·80	0·1655	0·000358
(vi)		41·21	4·79	0·1655	0·000359
(vii)	25 Aug., 1916	24·17	5·03	0·1638	0·000333
(viii)		24·46	5·05	0·1638	0·000332
(ix)	28 Aug., 1916	57·15	4·49	0·1676	0·000385
(x)		57·48	4·45	0·1676	0·000389
(xi)	29 Aug., 1916	25·14	5·03	0·1638	0·000337
(xii)		25·17	5·00	0·1638	0·000339

Table I, which shows one complete set of measurements for the vitreous disc 2, indicates the typical increase in conductivity which accompanies increase in the temperature of testing. This feature is common to both vitreous and crystalline preparations, as is shown in Table II.

Table II.—*Thermal Conductivity of Crystalline Selenium.*
Disc C, prepared at 180° C. on 15 June, 1916.
Thickness of disc = 0·5774 c m.

	Date.	Temperature of disc.	Thermal Conductivity	Electrical Conductivity (in arbitrary units)
I.	19 July, 1916	26·90 C.	0·00150	1·55
	20 July, 1916	35·69	0·00152	3·76
	21 July, 1916	46·01	0·00158	4·63
	24 July, 1916	26·37	0·00151	...
	25 July, 1916	52·61	0·00159	4·56
	26 July, 1916	27·05	0·00152	1·58
II.	15 Sept., 1916	32·44	0·00104	0·94
	18 Sept., 1916	41·10	0·00109	1·60
	19 Sept., 1916	52·59	0·00116	2·43
	20 Sept., 1916	32·41	0·00104	0·96
III.	3 July, 1917	28·48	0·00099	...
	4 July, 1917	56·46	0.00134	...
	5 July, 1917	27·19	0·00111	...
	6 July, 1917	27·16	0·00110	...

The relation between the temperature of measurement and the conductivity was found to be approximately linear. If we express the conductivity (K) at any temperature t by the equation

$$K_t = K_{25} [1 + (t - 25) a]$$

where K_{25} is the conductivity of that specimen at 25° C., the values of a range from 0·006 to 0·009 for the vitreous discs examined. For crystalline selenium a varied from 0·003 to 0·010, the upper limit being generally approached in the case of older discs.

In Table II are shown the summarized results for the crystalline disc C, illustrating the decrease in conductivity with the age of the specimen.

The values of the conductivity at 25° C. of all the vitreous discs prepared are collected in Table III. In the first three cases no special precautions were taken to remove impurities, but the fourth and fifth discs were prepared from highly purified selenium.[1]

Table III.—*Thermal Conductivity of Vitreous Selenium.*

Disc.	Age of Disc.	K_{25}
1	7 years	0·000328
2	5 days	0·000325
2 (retested)	1 year	0·000329
3	10 days	0·000293
3 (retested)	1 year	0·000300
4	10 days	0·000327
5	2 days	0·000312

These results suggest that the conductivity of vitreous selenium is independent of the age of the disc, and is not greatly affected by the presence of impurities. The variations which occur are possibly due to the existence of small traces of crystalline selenium in the vitreous discs.

[1] Prepared by R. Threfall, Proc. Roy. Soc. A. Vol. 97, p. 167, 1907.

The values of K_{25} obtained for crystalline selenium are given in Table IV.

Table IV.—*Thermal Conductivity of Crystalline Selenium.*

Disc.	Temp. of preparation.	I.		II.		III.	
		Age.	K_{25}	Age.	K_{25}	Age.	K_{25}
		Days.		Days.		Year.	
A	160°C.	11	0·00110	164	0·00081	1	0·00070
B	170	16	0·00157	134	0·00130	1	0·00097
C	180	38	0·00149	95	0·0099	1	0 00097
D	192	28	0·00161	148	0·00111	1	0·00120
E	200	9	0·00168	156	0·00120	1	0·00110
F	214	42	0·00183	...	...	1	0·00139

Two general tendencies are apparent, firstly the decrease in conductivity with the age of the disc, and secondly the increase in conductivity which accompanies an increase in the temperature of preparation. Departures from these general principles will be noted in the case of discs B and D (III). In preparation the former was heated for a longer period than any of the other discs, and, by accident, the bath was kept at a temperature of 57° C. for twenty-four hours shortly before the readings for D (III) were taken. This appears to have produced some permanent change in the substance, for when measured six weeks later the value of K_{25} for disc D was found to be 0·00119.

Table V has been included in order to illustrate what has previously been said with respect to the accuracy of the work. This disc, though apparently treated in exactly the same manner as the others, fails to give a linear relation between conductivity and temperature. The increase in the conductivity at room temperature is also very much larger than in the normal case shown in Table II.

The existence of such irregularities renders the numerical values of the conductivity unreliable, but there appears to be definite evidence that the thermal conductivity is

affected by factors which influence the electrical conductivity, in the manner stated at the beginning of this paper.

Table V.—*Thermal Conductivity of Crystalline Selenium.*
Disc D, prepared at 192° C. on 14 June, 1916.
Thickness of disc = 0·6749 c.m.

Date.	Temperature of disc	Thermal Conductivity.
6 July, 1916	26·64 C.	0·00162
7 July, 1916	34·22	0 00169
10 July, 1916	41·26	0·00168
12 July, 1916	27·11	0·00165
13 July, 1916	51·99	0·00175
18 July, 1916	25·77	0·00173

While the discs were in position for the thermal determinations, a few measurements of the electrical conductivity were made, typical figures being shown in Table II. The results may be summarised thus :—

(i) The temperature coefficient of the electrical conductivity is positive.

(ii) The conductivity of crystalline selenium is much greater than that of the vitreous form; it increases with the temperature of preparation, but decreases with the age of the disc.

(iii) In many cases irregularities in the value of the thermal conductivity are accompanied by corresponding, but more marked, variations in electrical conductivity.

These results indicate a close, though probably complex, relationship between the thermal and electrical conductivities, and are such as might be expected if the variations in the latter were due to changes in the number of free electrons present in the substance.

In conclusion, I wish to express my indebtedness to Professor O. U. Vonwiller, under whose direction this work was done, and to Mr. J. J. Forster B.Sc., for his assistance in taking the early measurements.

ELASTIC PROPERTIES OF SELENIUM.

NOTES on the ELASTIC PROPERTIES of SELENIUM.

By O. U. VONWILLER, B.Sc.

IN 1916 the writer performed some experiments primarily with the object of determining elastic constants of selenium. The investigation was not carried far before it had to be given up, mainly on account of lack of time, but some qualitative results were obtained which appear to be of sufficient interest to be recorded; among these is a light effect not noticed before.

Thin threads of vitreous selenium were prepared by dipping the end of a glass rod into molten selenium and withdrawing it fairly rapidly. It was found that, unless the temperature of the liquid were too high—in which case threads could not be drawn on account of the great fluidity of the substance—long threads were produced without difficulty; these invariably contained numerous inequalities in thickness, but usually it was possible to obtain several pieces 10 centimetres or more in length, of fairly uniform section, the diameter being generally about 0·04 centimetre. These threads seemed to consist wholly of vitreous selenium no trace of the crystalline modification being visible.

In endeavouring to determine Young's modulus, methods of bending were first used; in some cases a thread was supported near its ends and loaded in the middle by means of bent pieces of thin wire placed on a light wire hook hanging at the central point, while in others one end of the thread was held between a pair of metal jaws lined with paper to prevent crushing, and loaded by a metal rider placed near the free end, the depression, on loading, of the

centre or end of the thread being measured with the aid of a microscope mounted on a vertical screw.

It was found that the behaviour of the selenium resembled that of such substances as pitch and sealing-wax, the application of a load resulting in an immediate depression, which increased continuously as long as the load was applied; upon removal of the load there was an immediate partial recovery and a further gradual rise lasting for a time, depending on the magnitude and duration of the load, the total recovery never equalling the total depression. Gradual and continuous bending took place without any load other than the weight of the thread itself.

Observations made at various times for a week on one thread, showed that the magnitude of the viscosity effect, that is the continuous movement under the application of a steady load, depended on the illumination. This thread was 9·5 cm. long, about 0·04 cm. in diameter, and was supported on two brass cylinders 0·7 cm. in diameter, placed 8·5 cm. apart, no external load being applied. It was noticed that, while the fall of the central point was continuous, the rate of movement was much less in the night than during the day when the selenium was illuminated by diffused daylight. That this effect was not due directly to temperature changes alone, was shown by darkening the room during the daytime when the rate of fall was found to decrease. At the end of the week the rate of fall was practically the same as at the beginning under like conditions; in this time the originally straight thread had been bent to form an arc, the central point of which was 0·9 cm. below the straight line joining the ends.

Experiments with several other pieces of selenium gave similar results; below are given some of the readings obtained in the case of a short thread of average diameter 0·041 cm., one end of which was fixed while a rider of mass

0·06 gm. was applied near the free end, the distance between rider and support being 5·3 cm.   In one trial the depressions of the free end observed at various times after the first application of the load were :

Time.	Depression.
40 seconds ·	0·1287 cm.
80 ,,	0·1330 ,,
190 ,,	0·1377 ,,
495 ,,	0·1460 ,,

while when the load was removed after being applied for 9 minutes, the recovery was as follows :

Time.	Recovery.
40 seconds	0·1176 cm.
120 ,,	0·1286 ,,
180 ,,	0·1322 ,,
315 ,,	0·1384 ,,

The effect of light upon the continuous fall is shown in Table I, where readings are given for several days during the whole of which the load was applied.

When the load was finally removed after being applied for four days, the usual effects were observed, a rapid initial recovery being followed by a gradual rise, which in this case was still perceptible after 25 minutes.

It is seen that the average fall per minute, given in the fourth column, is invariably much greater for periods of illumination than for those of darkness. When the room was darkened after the selenium had been exposed to light, the rate of fall did not drop suddenly but decreased gradually for several hours, as is seen clearly in the readings of 10th April. A corresponding lag occurs in the increase in rate of fall when the selenium is illuminated after having been in the dark, but this change is established in a much shorter time than the other. It is very likely that the viscosity varies with temperature changes, but it is certain

that the changes in the rate of fall, due to illumination, in the cases examined, were much greater than those due to the small variations which took place in temperature.

Table I.

Date. 1916 April	Time.	Reading cm.	Rate of Fall 10⁻⁶ cm. per min.		Temp ° C.
7th	4·30 p m.	2 9286			21·4
			129	Dark	
·8th	9·10 a m.	2 7995			21·2
			471	Light	
„	12 09 p.m.	2·7151			21·2
			59	Dark	
10th	9·30 a.m.	2·5534			20·7
			304	Light	
„	11·08 a.m.	2·5236			21·2
			261	Light	
„	1·09 p.m.	2·4917			21·0
			201	Dark	
„	2·13 p.m.	2·4788			21·0
			145	Dark	
„	3·40 p m.	2·4622			21·0
			98	Dark	
„	4·34 p.m.	2·4609			20·8
			62	Dark	
11th	9·45 a.m.	2·3970			20·5
			167	Light	
„	10·03 a.m.	2·3940			20·8
			225	Light	
„	11·11 a.m.	2·3787			20·9
			261	Light	
„	12·05 p.m.	2·3646			21·0
			163	Dark	
	1·10 p.m.	2·3540			21·1
			126	Dark	
„	2·07 p.m.	2·3468			21·0
			128	Dark	
„	3·33 p.m.	2·3358			21·2

In the example recorded the intensity of illumination probably varied considerably at different times as diffused daylight was used, so that comparisons may not be made of the various results obtained in the light. At the time

these measurements were made a new electric light instal-
lation was being erected in the Physical Laboratory, and
it was not possible to secure satisfactory artificial illumin-
ation of constant intensity for any prolonged period.

Some trials made with threads shortly after their pre-
paration showed that the viscous movement was much
greater than with older specimens; for example, a thread
held at one end without any load was first examined 15
minutes after being drawn; the free end was observed to
fall as follows:

in 10 minutes 0·104 cm.
     20   ,,   ·184 ,,
     30   ,,   ·246 ,,
     60   ,,   ·376 ,,

A fortnight later it was found that in $1\frac{1}{4}$ hours the fall
was only 0·058 cm.

Owing to the viscosity effect it was not possible to obtain
a satisfactory value of Young's modulus by bending methods
but the readings obtained indicated that it was of the
order of 3×10^{10} dynes per sq. cm. It seemed probable
that more trustworthy results would be obtained by a
method of direct extension, and an attempt was made with
a thread of vitreous selenium about 22 cm. long and of
average diameter 0·0430 cm., the upper end of which was
held in a clamp while a light scale pan was attached by
thin wires and sealing-wax to the lower end. By means
of two microscopes the movements of two points, one near
the upper and one near the lower end, were observed upon
the application of a load. The movement of the upper
point was always very small and was read with the aid of
a scale in the eye-piece of the upper microscope while the
lower microscope was moved on a vertical screw. With
the exception of a few millimetres at each end the whole

length of the thread could be shielded from light by a brass cylinder blackened on the inside. A narrow longitudinal slit and radial slits in the closed ends enabled the cylinder to be removed without disturbing the thread or its attachments, so that an exposure to light could be made when desired.

Readings with loads of from 0 to 50 gm. showed that Hooke's law was followed, and that with the load applied for several minutes the reading did not change appreciably. A number of readings made with a load of 50 gm. alternately applied and removed, with the thread in darkness and exposed to light, gave a mean extension of 0·0143 cm. in a length of 20·7 cm., and any difference on illumination was certainly less than the probable error of this extension, about 0·0003 cm. The value of Young's modulus calculated from these observations is $4·89 \times 10^{10}$ dynes per sq. cm., but it must be noted that only one thread was examined in this way so that no great weight should be attached to the numerical result. The mean temperature of these observations was 20°·8 C.

When the load was allowed to remain for a prolonged period it was found that the extension gradually and continuously increased, and observations made when a load of 50 gm. was applied continuously for a week showed that the movement was more rapid when the selenium was illuminated than when it was in darkness. Although the rate of movement was very small and some uncertainty exists as to the coefficient of expansion of the material, the light effect was unmistakeable, and the ratio of movement in darkness to that in light seems to be of the same order as in the earlier experiments. The total increase in length in the week was 0·06 cm.

In order to ascertain whether crystalline selenium possessed similar mechanical properties, endeavours were

made to produce threads of the substance in this form. Considerable difficulty was met, but a few satisfactory preparations were made by placing threads of vitreous selenium on a horizontal sheet of mica in a closed heating oven, the temperature of which was slowly raised to about 180° C., the time occupied in the heating being about two hours. Generally after the heating the thread was found to be broken into very short lengths, but several good pieces were obtained. Very great care was needed in handling these preparations as they are extremely fragile and threads were frequently broken before any satisfactory readings were obtained.

As with the vitreous selenium, it was found that the application of a load to the end of a "beam" of crystalline selenium resulted in an immediate elastic depression followed by a gradual fall with continued application of the load; this gradual fall, however, in all cases was much smaller than with vitreous selenium under corresponding conditions. The viscosity effect is much greater shortly after removal of the thread from the heating oven, decreasing for several hours. A few observations were made with threads prepared at different temperatures, ranging from 179° C. to 197° C., but it is impossible to say, from them, how the effects depend on the temperature of preparation.

With crystalline selenium light appears to have no influence on the immediate elastic depression due to loading and it has been impossible to detect any difference, due to change of illumination, in the rate of movement under continued application of a load. However, as the rate of movement was always very small and as the threads broke before a long series of readings could be made, the failure to detect a light effect on the viscosity of crystalline selenium must not be taken as conclusive evidence that it does not exist or even that it is very small.

Summary of Results.

Thin threads of vitreous selenium tested by methods of bending and of direct extension, show mechanical properties similar to those of viscous solids, such as pitch and sealing-wax, the first application of a load causing an immediate elastic strain, while the continued application results in a continually increasing permanent deformation.

Similar effects are observed with crystalline selenium, but the viscosity effect is relatively very much smaller.

In the case of preparations of vitreous selenium the viscosity effect, the gradual movement under continued application of a load, is found to depend upon the illumination, the rate of movement being greater when the selenium is exposed to light than when it is in the dark; the response to change of illumination is not instantaneous, the rate decreasing for several hours, when a change is made from diffused daylight to darkness.

No such light effect has been detected with preparations of crystalline selenium. The observations made on these are, however, less satisfactory than those on threads of vitreous selenium.

With threads both of vitreous and of crystalline selenium the viscous movement is much greater shortly after preparation than a few hours later.

A test by direct extension of a thread of vitreous selenium gives a value for Young's modulus of 4.89×10^{10} dynes per sq. cm. at $20°.8$ C.

VOLUME CHANGES IN THE PROCESS OF

SOLUTION

VOLUME CHANGES IN THE PROCESS OF SOLUTION.

By GEORGE JOSEPH BURROWS, B.Sc.

(Communicated by Prof. C. E. Fawsitt.)

A considerable amount of work has been recorded on the changes in volume which take place in the formation of solutions. When a solid is dissolved in a liquid, or when two liquids are mixed, the volume of the resultant solution is found in most cases to differ from the sum of the original volumes of the constituents. We cannot state how far this is due to a change in the volume of the solute and how far to the solvent. For the sake of convenience it is customary to assume that the volume of the solvent is unaltered by the process of solution, and to attribute any change in the volume of the system to the solute. In this way the volume of a solute in a solution may be determined.

Thus if A represents the weight in grams of solute dissolved in 100 grams of solvent,

d_0 = the density of the pure solvent,

d_1 = the density of the solution,

and v_s = the specific solution volume of the solute,

then, $v_s = \left(\dfrac{100 + A}{d_1} - \dfrac{100}{d_0} \right) \div A$ .... (I)

or if ϕ = the molecular solution volume of the solute,

then, $\phi = \dfrac{M + g}{d_1} - \dfrac{g}{d_0}$ .... (II)

where g = the weight in grams of solvent containing the molecular weight (M) in grams of solute.

By employing the above formulæ Tyer[1] and Dawson[2] have shown that the specific (or molecular) solution volume

[1] J.C.S., (1910) 97, 2620.   [2] *Ibid.*, 1896.

of a solute varies slightly in different solvents, the order of variation in most cases being the same as that of the compressibility of the solvent. In cases where the process of solution is accompanied by no change in the molecular complexity of both solute and solvent the specific solution volume is found to be practically independent of concentration. In aqueous or alcoholic solutions, however, it has been repeatedly shown that the specific volume of the solute varies with its concentration. The results recorded in the present paper were obtained chiefly from experiments with solutions in water or alcohol, or in mixtures of these solvents. All the reagents used in this investigation were purified by suitable means, and their final purity determined by physical methods, e.g., density, melting point or boiling point. The solutions were all prepared by weighing both solute and solvent. The density of the solvent or solution was determined by means of a pyknometer of capacity about 22 cc. Before adjusting the volume of the liquid in the pyknometer it was allowed to remain suspended for about an hour in a thermostat, the temperature of which was maintained constant to $0·05°$ C. All weighings were reduced to vacuo.

Aqueous Solutions.

In the following tables, A represents the concentration of solute in grams per 100 grams of solvent, d_0 the density of the pure solvent, d_1 the density of the solution, v_s the specific solution volume of the solute (Equation I), and ϕ the molecular solution volume of the solute (Equation II). The temperature is stated in each case.

Table I.

Potassium chloride in water ($d_0 = ·997073$). Temp. 25° C.

A	d_1	v_s	ϕ
·1637	·998117	·361	26·92
·4221	·999775	·358	26·71

Table I.—*Continued.*

A	d_1	v_s	ϕ
1·1491	1·004265	·371	27·65
2·1030	1·010137	·373	27·84
5·2017	1·028575	·382	28·48
8·2830	1·046080	·389	29·00
11·6167	1·064402	·393	29·35
20·0902	1·107547	·405	30·21
26·7036	1·138501	·412	30·72

Table II.

Mercuric chloride in water.   Temp. 25° C

A	d_1	v_s	ϕ
·2981	·999468	·194	52·74
·3593	·999983	·188	50·92
·8301	1·003829	·183	49·63
1·8639	1·012268	·180	48·84
3·0954	1·022273	·180	48·68
3·9302	1·029027	·179	48·64
5·4144	1·040988	·179	48·60

Table III.

Saccharamide in water.   Temp. 25° C.

A	d_1	v_s
·09474	·997521	·527
·38925	·998861	·540

Table IV.

Succinic acid in water.   Temp. 25° C.

A	d_1	v_s	ϕ
0·9192	·999803	·702	82·90
2·3348	1·003930	·703	82·95
3·5546	1·007314	·706	83·33
3·8726	1·008090	·709	83·69

Table V.

Succinamide in water.   Temp. 25° C.

A	d_1	v_s	ϕ
·1730	·997450	·783	91·00
·2229	·997607	·761	88·46
·3547	·997892	·770	89·42

Table VI.

Tricarballylamide in water. Temp. 25° C.

A	d_1	v_{κ}	ϕ
·1853	·997611	·710	123·0
·3235	·997984	·719	124·5
·4729	·998462	·706	122·3
·5916	·998757	·715	124·0
1·3564	1·000989	·710	122·9
1·9499	1·002696	·709	122·8
2·2798	1·003636	·709	122·8

Table VII.

Carbamide in water. Temp. 25° C.

A	d_1	$v_{\star}$	ϕ
2·6329	1·003912	·737	44·27
5·0484	1·009800	·738	44·36
7·3010	1·015198	·740	44·47
14·4848	1·030884	·743	44·66
33·0611	1·064318	·748	44·96
53·8893	1·093286	·751	45·14

Table VIII.

Carbamide in water. Temp. 30° C.

A	d_1	v_{κ}	ϕ
2·3290	1·001575	·744	44·72
9·0567	1·017457	·745	44·76
15·4282	1·030922	·747	44·88

Table IX.

Acetamide in water. Temp. 30° C.

A	d_1	v_{δ}	ϕ
4·5875	·998254	·945	55·84
7·5278	·999892	·944	55·76
10·1471	1·001300	·943	55·72
16·7179	1·004590	·942	55·66

The specific volume of liquid acetamide[1] at 30° C. is ·956.

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[1] Meldrum and Turner, J.C.S., 1908, 93, 876.

Table X.
Propionamide in water.   Temp. 30° C.

A	d_1	v_4	ϕ
1·8533	·996096	·981	71·72
3·9972	·996593	·980	71·65

The specific volume of liquid propionamide[1] at 30° C. is 1·000.

Table XI.
Sucrose in water.   Temp. 30° C.

A	d_1	v_4	ϕ
2·7695	1·006078	·619	211·9
4·5190	1·012373	·621	212·6
8·2459	1·025524	·621	212·6

The specific volume of liquid sucrose at 30° C. is ·661.[2]

It will be noticed from the foregoing tables that the value of v_4 or of ϕ varies with the concentration in nearly every case. The effect of concentration is most marked in the case of electrolytes ; thus in the case of potassium chloride the value of v_4 increases by 14 per cent. from $A = ·16$, to $A = 27$. But even in the case of non electrolytes, such as carbamide, the specific solution volume is not constant but increases with concentration. In the case of mercuric chloride and of acetamide, the solution volume decreases with concentration.

The above results are similar to those obtained by various authors for other solutes in aqueous solution. In general it has been found that the solution volume increases with the concentration of the solute, the effect being most marked in the case of strong electrolytes. This variation of v_4 with A in the case of aqueous solutions (and of solutions in other solvents containing hydroxyl group) has been attributed chiefly to two causes :

   (a) the formation of hydrates (or solvates)
   (b) in the case of electrolytes to the variation in the degree of dissociation of the solute.

[1] Meldrum and Turner,   [2] Schwers, J.C.S., 1911, 99, 1478.

There is a considerable amount of evidence now available indicating the existence of solvates in solution. Furthermore Tyer[1] has shown that in certain cases e.g., calcium chloride in ethyl alcohol, in which there is little doubt that the calcium chloride exists in solution as $CaCl_2, 4 C_2H_5OH$, increasing concentration is accompanied by a marked increase in the specific solution volume of the solute, due to a decrease in the degree of solvation with increasing concentration of solute. These results would indicate that the variation of v_s with concentration observed in aqueous solutions even in the case of non-electrolytes is due also, in part at least, to the formation of solvates.

The solution volumes of many strong electrolytes in water have been determined by various authors, and their results show that the specific volume increases with concentration. In certain cases, e.g., magnesium sulphate, if the value of A be sufficiently reduced v_s may even become negative, indicating that the volume of the solution is less than that of the water used. The effect of concentration varies considerably with different electrolytes, being far more marked for instance in the case of sodium chloride than with magnesium sulphate. This decrease of v_s with dilution has been attributed to the effect of increasing dissociation of the solute. The observed decrease in v_s cannot be attributed entirely to a decrease in the actual specific volume of the solute. The fact that in certain cases a negative value is obtained for v_s indicates that in these cases the water is appreciably contracted in the process of solution. As Tyer has already pointed out, it is quite probable that in aqueous solutions of electrolytes, the ions of the solute cause a condensation in the volume of the water molecules. But there is apparently no proportionality between the degree of dissociation of an electrolyte and its specific solution volume.

[1] J.C.S., 1911, 99, 871.

In discussing the variation of the specific solution volume with concentration of solutes in aqueous or alcoholic solutions, one other factor has been constantly overlooked. The formulæ (Equations I and II) from which the solution volume of a solute is calculated, must give rise to regular variations of v_s or ϕ with A, in all cases where the volume of the solvent is altered by the process of solution. In the above equations, if the solvent contracts during the process of solution, this contraction is attributed wholly to the solute. Thus in the equation:

$$v_s = \frac{\dfrac{100 + A}{d_1} - \dfrac{100}{d_0}}{A} \quad \dots\dots\dots\dots\dots\dots\dots(I)$$

the term $\dfrac{100}{d_0}$ is taken to represent the volume of 100 grams of water in all solutions, no matter what the concentration of the solute may be. These formulæ are strictly applicable only in the investigation of solutions of the same solute in different solvents. Thus if solutions of a certain solute in two different solvents be prepared, and the solution volume of the solute in each be calculated, the relative values of v_s or ϕ, may in these cases be taken to represent the relative volume changes in the system solute-solvent. Results obtained in this way afford us information as to the relative order of volume changes produced by dissolving a certain solute in different solvents. But the formulæ are not applicable to the study of the effect of different concentrations of a solute in a particular solvent. It is quite illogical to assume that the volume of one constituent of a solution is unaltered over a wide range of concentrations and then to attempt to explain the variations in the volume of the other constituents, deduced by means of this assumption. Let us consider for example, two solutions of a certain solute in water, in both of which A is small, but in one case much greater than in the other. Furthermore, we will assume that the process of solution causes a con-

traction in the volume of the water, and also that although the actual volume of the latter in both cases is less than $\frac{100}{d_0}$ it is sensibly the same in both solutions.

In calculating the specific solution volumes of these solutions according to Equation I, it follows that in both cases v_s would be less than the actual volume occupied by one gram of the solute in the solution, and furthermore, the error so obtained would decrease with increasing values of A. Even in a case where the actual specific volume of the solute was constant and independent of its concentration, the values found for v_s would increase with A. We cannot infer, therefore, that because the values of v_s are found to vary in a definite direction with concentration, the actual specific volume of the solute varies in this direction, or indeed that there is any variation at all. This particular point can be well illustrated by considering a solution formed by mixing two liquids, e.g., formamide and water, in which the formamide is considered the solute and the water the solvent. The formamide used in these experiments was purified by the method of Köhler,[1] by standing over anhydrous sodium sulphate from which it was distilled under reduced pressure. The density of the pure amide at 25° C. was 1·13126. The densities of the solutions were determined both at 20° C. and 25° C. and the specific solution volume of the formamide in water calculated in the usual way. In addition, the contraction per cc. of the original volume was determined by subtracting the volume of the solution from the sum of the volumes of the constituents, and dividing this difference by the original volume of the constituents. Thus if x represents the volume of formamide, y the volume of water, and z the resulting volume of the solution, then the specific contraction $\triangle_v$ is given by:

$$\triangle_v = \frac{(x + y) - z}{(x + y)}$$

Table XII.—Formamide in water.

Per cent conc. of Formamide.	A	Temp. 20° C.			Temp. 25° C.		
		d_1	v_s	$\triangle_v$	d_1	v_s	$\triangle_v$
0·73	0·7392	0·999321	·8515	·000212	·998136	·8561	·000203
1·70	1·7251	1·000858	·8467	·000576	·999558	·8559	·000475
4·10	4·2770	1·004545	·8482	·00134	1·003115	·8556	·00116
14·73	17·274	1·020458	·8536	·00405	1·018188	·8598	·00362
25·70	34·584	1·036469	·8580	·00601	1·03397	·8637	·00537
37·11	59·016	1·05254	·8625	·00705	1·04963	·8676	·00632
46·52	86·976	1·06541	·8660	·00722	1·06226	·8706	·00655
59·05	144·229	1·08216	·8702	·00663	1·07859	·8716	·00594
66·86	201·709	...		..	1·08874	·8766	·00532
75·94	315·699	1·10408	·8753	·00446	1·10020	·8792	·00401
88·27	752·19	1·11979	·8786	·00206	1·11580	·8820	·00191
94·82	1831·6	1·12846	·8799	·000859	1·12427	·8833	·000745
97·48	3863·1	1·13204	·8803	·000394	1·12783	·8837	·000347
99·77	42160·0	1·13507	·8807	...	1·13090	·8840	...
100·00	...	1·13552	·8807	...	1·13126	·8840	..

It will be seen from the above table, that whereas the value of v_s increases with concentration for solutions containing more than one per cent formamide, the actual specific contraction of the system also increases up to 44 per cent. formamide and then decreases (Fig. 1). Between these concentrations therefore, the values of v_s would lead to the inference that the specific volume of the system increased with concentration, whereas the reverse is really the case.

Similar conclusions can be drawn from results obtained by mixing ethyl alcohol with water, and considering the solution as one of alcohol in water. The results obtained in this case are given in the following table.

Table XIII.
Ethyl alcohol in water. Temp. 30° C.

Per cent. alcohol.	A	d_1	v_s	$\triangle_v$
0	—	—	—	—
25·44	34·1123	·955387	1·1708	·02602
30·47	43·8186	·946572	1·1754	·02952
36·62	57·7890	·934695	1·1832	·03231
47·11	89·0805	·912305	1·1992	·0339
58·89	143·232	·885436	1·2167	·03233
100·00	...	...	1·2808	...
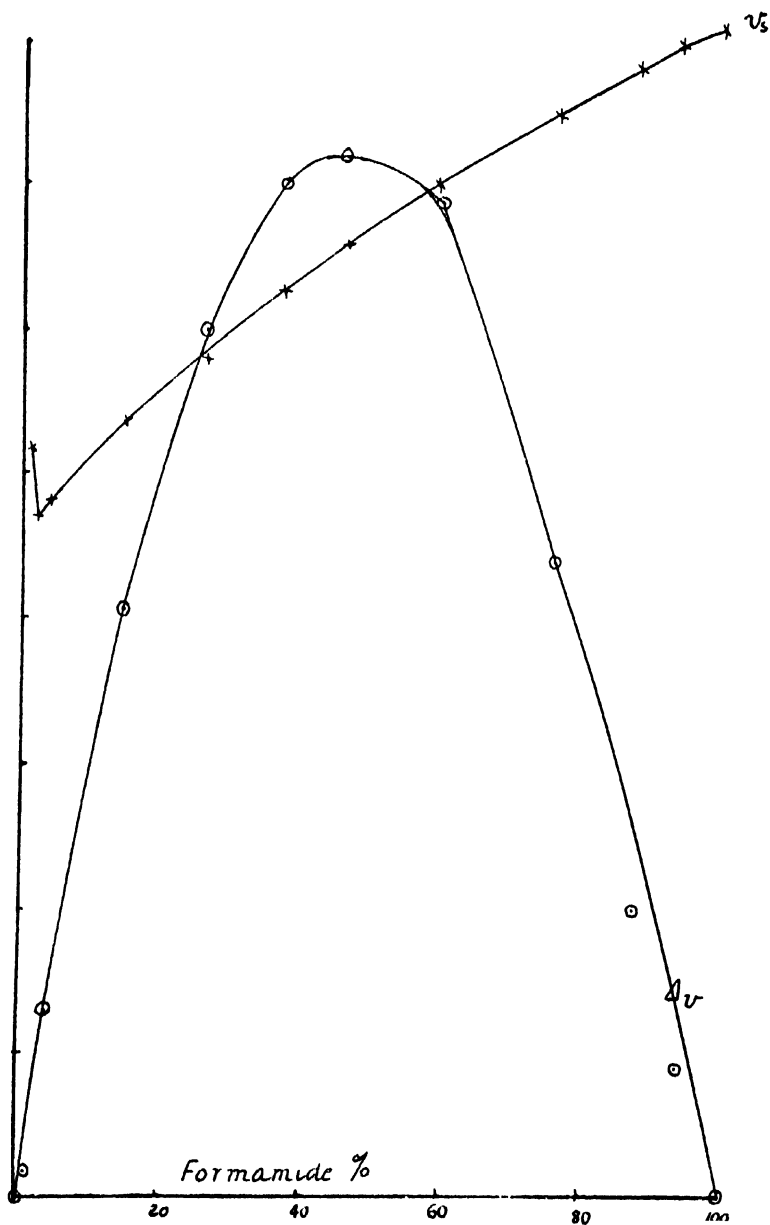
Fig. 1.   Formamide and Water (20°c)

Here the value of v_s increases regularly with concentration, whilst the specific contraction also increases up to 47.1 per cent. and then decreases. In these two cases the variation of v_s with A cannot be interpreted as indicating an increase in the specific volume of the system with increasing concentration of the solute. It follows, therefore, that a comparison of v_s with A is likely to lead to incorrect conclusions. Thus in the examples given above, since the specific volume of the solvent is considered constant throughout the series ($= \dfrac{1}{d_0}$) and v_s is found to increase with A one would naturally conclude that the specific volume of the system as a whole increased with concentration of the solute, whereas we know that up to a certain concentration in each case it decreases.

There is no reason to doubt that the same is also true for solutions of solids in water. In the case of sucrose solutions at least, similar results have been obtained. Thus in Table XI, the values under v_s are constant within the limits of experimental error, and yet by measuring the actual contractions in the formation of aqueous sucrose solutions, Schwers[1] has shown that the specific volume of the system as a whole decreases with increasing concentration up to 70 per cent. sucrose. These results show that the application of Equations I or II in considering the effect of the concentration of the solute on its solution volume is apt to lead to erroneous conclusions.

From an exhaustive study of the molecular solution volumes of homologous series, Traube[2] found that certain values could be assigned to the solution volumes of the different atoms. The "molecular volume" is equal to the sum of the atomic volumes together with the "molecular

[1] J.C.S , 1911, 99, 1478.

[2] Zeit. anorg. Chem. 1895, 8, 838   Ber., 1895, 28, 2728, 2924, Ber., 1896, 29, 1023; Ber. 1897, 30, 265

co-volume" which represents the additional volume occupied by the molecule by virtue of its vibrations. The molecular solution volume $_sV_m$ may therefore be expressed by

$$_sV_m = \Sigma n\, V_a + \triangle$$

where $\Sigma n\, V_a$ is the sum of the atomic volumes and $\triangle$ the molecular solution co-volume, which Traube found to be approximately constant for all classes of compounds, the mean value at 15° C. being 12·4 ccs. Thus the following values were obtained for atomic volumes at 15° C.:—C = 9·9 H = 3·1, O(OH of COOH) = 0·4, O(OH) = 2·3, O(CO) = 5·5, N = 1·5, $\triangle$ = 12·4.

In the following table the values under ϕ are those determined experimentally (Tables IV — XII), and those under $_sV_m$ are the values calculated from the atomic volumes at 15° C. (Traube).

Table XIV.

	ϕ	$_sV_m$ (15° C.)
Formamide (25° C.) HCONH$_2$	38·9	38·6
Acetamide (30° C.) CH$_3$CONH$_2$	55·8	54·7
Propionamide (30° C) C$_2$H$_5$CONH$_2$	71·7	70·8
Carbamide (25° C) CO $\begin{matrix} NH_2 \\ NH_2 \end{matrix}$	44·4	43·2
Succinamide (25° C) (CH$_2$CONH$_2$)$_2$	89·4	90·8
Succinic acid (25° C) (CH$_2$COOH)$_2$	83·0	82·4
Tricarballylamide (25° C)	124·0	126·9

The agreement between the experimental and calculated values is satisfactory; the difference between the values is no doubt due to the increase in value of $\triangle$ with temperature.

Solutions in ethyl alcohol.

The specific and molecular solution volumes of several amides in alcoholic solution were determined at 30° C. The results obtained are given in the following table.

Table XV.

Solvent—Ethyl alcohol (d_0 = ·780777).   Temp. 30° C.

(a) Formamide.

A	d_1	v_s	ϕ
1·8454	·785604	·846	38·14
6·1292	·796280	·849	38·25
18·5815	·823708	·855	38·52

(b) Acetamide.

4·3441	·789723	·932	55·07
7·0327	·794941	·933	55·15
9·6461	·799847	·934	55·16

(c) Propionamide.

3·2024	·786515	·980	71·62
7·5389	·793896	·979	71·55
11·4767	·799920	·983	71·86

(d) Butyramide.

2·6969	·785056	1·015	88·41
5·9635	·789912	1·018	88·65

(e) Capronamide.

2·2745	·783658	1·069	123·10
3·4050	·785038	1·069	123·17

The values of v_s for any particular solute are fairly constant and independent of concentration. If we subtract the molecular volume of one amide from the next higher homologue in the series, the difference in volume corresponding to an addition of CH_2 to the molecule can be calculated. These results are given below.

Table XVI.

Amide.	ϕ	$\Delta\phi$
$HCONH_2$	38·3	...
CH_3CONH_2	55·1	16·8
$C_2H_5CONH_2$	71·7	16·6
$C_3H_7CONH_2$	88·5	16·8
$C_4H_9CONH_2$	...	...
$C_5H_{11}CONH_2$	123·1	2 × 17·3
	Mean	17·0

It will be noticed that $\triangle_\phi$ is approximately constant up to butyramide, but between this member and the next there is a considerable increase in volume difference. This variation for higher members of an homologous series is common to most physical properties.

Mixed Solvents.

Determinations were also made of the solution volumes of different solutes in solvents prepared by mixing two liquids. Weighed quantities of the liquids were mixed and the density of the mixture determined with a pyknometer in the usual way. A weighed quantity of the solute was then dissolved in a weighed quantity of the mixture, and the density of this solution determined, and the specific solution volume of the solute calculated in the usual way. In the following table are given the solution volumes of benzophenone in various solvents at 30° C.

Table XVII.

Solute —Benzophenone. Temp. 30 C.

(a) Solvent — Benzene ($d_0 = \cdot868327$).

A	d_1	v_s
1·5067	·871189	·897
4·2746	·876398	·893
12·4329	·890517	·892

(b) Solvent—Acetone ($d_0 = \cdot781169$).

3·6851	·790169	·870
7·5410	·798813	·872
11·9758	·808462	·873

(c) Solvent—Ethyl alcohol ($d_0 = \cdot780897$).

7·7015	·798935	·876
11·8189	·807776	·877

(d) Solvent—Benzene-Acetone, Acetone = 50·72% (weight)
$d_0 = \cdot822244.$

5·8368	·835038	·878
12·9402	·848865	·883

(e) Solvent—Alcohol-Acetone, Acetone = 56·36% (weight)
$d_0 = \cdot781568.$

10·1467	·804867	·877
13·2029	·811255	·878

For the sake of comparison the specific volume of the
pure solute in the liquid state was also determined. Benzo-
phenone is solid at the ordinary temperature, having a
melting point of 48°·5 C. If, however, liquid benzophenone
be allowed to cool without shaking, it is possible to keep
it liquid for a considerable time below 30° C. The volume
of the liquid benzophenone was determined by carefully
filling a five cc. pyknometer with the molten material, from
which air had been removed as completely as possible by
means of a suction pump, and then cooling carefully in the
thermostat and adjusting the volume in the usual way.
With a little care the liquid could be kept without crystal-
ising till after the adjustment, and the volume accurately
determined.   One determination gave for the density of
liquid benzophenone, $d_{30} = 1·10231$ whence $v = 9072$. A
duplicate experiment gave $v = ·9070$.

It will be seen from Table XVII that the specific solu-
tion volume is less in any of the solvents than the specific
volume of the liquid solute, indicating that the process of
solution is accompanied by contraction in each of these
cases.   The specific volume is greater in benzene than in
either acetone or alcohol. This is in agreement with the
results obtained by Tyrer *(loc.cit.)* for other solutes in these
solvents.   The values of v_s for solutions in the benzene-
acetone mixture are intermediate between the values
obtained in the pure solvents.   In the case of the acetone-
alcohol solutions, the values of v_s are almost identical with
those for solutions in pure alcohol.   In the preparation of
both of these "mixed solvents" there is practically no
change in volume.   Thus in the preparation of the benzene-
acetone mixture, 145·3922 cc. of benzene at 30° C. were
mixed with 166·3833 cc. of acetone at 30° C., and the final
volume was 311·5620 cc. at 30° C.   The total contraction
was only 0·2135 cc. which corresponds to a specific con-

traction per cc. of the original volume of $\Delta_v = \cdot000685$ cc.
Similarly for acetone-alcohol, $\Delta_v = \cdot000842$. These results
point to the conclusion that in mixtures of organic liquids
such as the above, in the preparation of which there is
practically no change in volume, the specific solution
volume of a solute lies between its values in the simple
solvents.   It will be seen from the following tables that
this is not the case with solutions in water-alcohol mixtures.
In Table XVIII are given the specific solution volumes of
mercuric chloride in water, ethyl alcohol, and in a mixture
of alcohol and water, at 30° C.

Table XVIII.

Mercuric chloride.

(a) In water ($d_0 = \cdot997062$).

A	d_1	v_s
2·1396	1·013096	·180
3·6307	1·025072	·182

(b) In ethyl alcohol ($d_0 = \cdot780897$).

7·2830	·830233	·160
13·2739	·870108	·160
22·9652	·933074	·162

(c) In water-alcohol ($d_0 = \cdot941605$).

Alcohol $= 33\cdot17$ per cent. (weight).

2·8875	·963672	·196
6·1069	·987959	·196
7·0298	·994844	·197

The solvent used in this case was prepared by mixing
88·1129 cc. of water with 55·7538 cc. of alcohol.   The
resulting volume was 139·4110 cc., which corresponds to a
contraction of 4·4557 cc. or ·03097 cc. per cc. of the original
volume.   This contraction is about fifty times as great as
that observed in the case of benzene-alcohol or benzene-
acetone,

It will be noticed in the preceding table that the value of v_s is greater in the mixture than in either of the simple solvents. This was found to be the case with all solutes whose specific volumes were determined in water-alcohol mixtures, several examples are given in the following tables. The specific contraction Δ_v observed in the preparation of the different mixtures used as solvents is stated in each case. The percentages of alcohol given are by weight.

Table XIX.

Solute—Carbamide   Temp 25° C.

(a) In water (d_0 = ·997073.

Δ	d_1	v_s
2·6329	1·003912	·737
5·0484	1·009800	·738
7·3010	1·015198	·740
14·4848	1·030884	·743

(b) In ethyl alcohol (d_0 = ·785211).

2·4796	·794191	·677
2·8160	·795421	·678
3·5211	·797950	·676
5·4320	·804559	·679

(c) In water-alcohol (24·44 per cent. alcohol).

d_0 = ·959875 Δ_v = ·0255 cc.

2·3307	·965917	·756
5·4357	·973611	·757
11·8262	·988369	·758

(d) In water-alcohol (35·70 per cent. alcohol).

d_0 = ·940129 Δ_v = ·0326 cc.

1·19700	·945452	·754
3·5158	·949373	·759
6·8602	·957711	·760
9·8484	·964845	·760
13·5561	·973289	·760

(e) In water-alcohol (44·17 per cent. alcohol).

d_0 = ·922752 Δ_v = ·0345 cc.

A	d_1	v_s
3·3277	·931880	·754
6·7110	·940644	·756
9·8411	·948375	·757
15·7980	·962235	·758

(f) In water-alcohol (66·13 per cent. alcohol).

d_0 = ·872753 Δ_v = ·0305 cc.

2·7611	·881119	·741
5·3457	·888744	·740
6·4242	·891689	·743
10·7088	·903470	·743

(g) In water-alcohol (75·50 per cent. alcohol).

d_0 = ·850251 Δ_v = ·0258 cc.

3·5510	·861364	·734
5·6643	·867714	·735
6·9366	·871478	·734
9·9906	·880130	·737

If the values of v_s in Table XIX be compared for the same concentration of solute, the variation of the specific solution volume with the composition of the solvent is more clearly shown. The values of v_s for $A = 6$ are given below, together with the specific contraction observed in the preparation of each of the solvents.

Table XX.

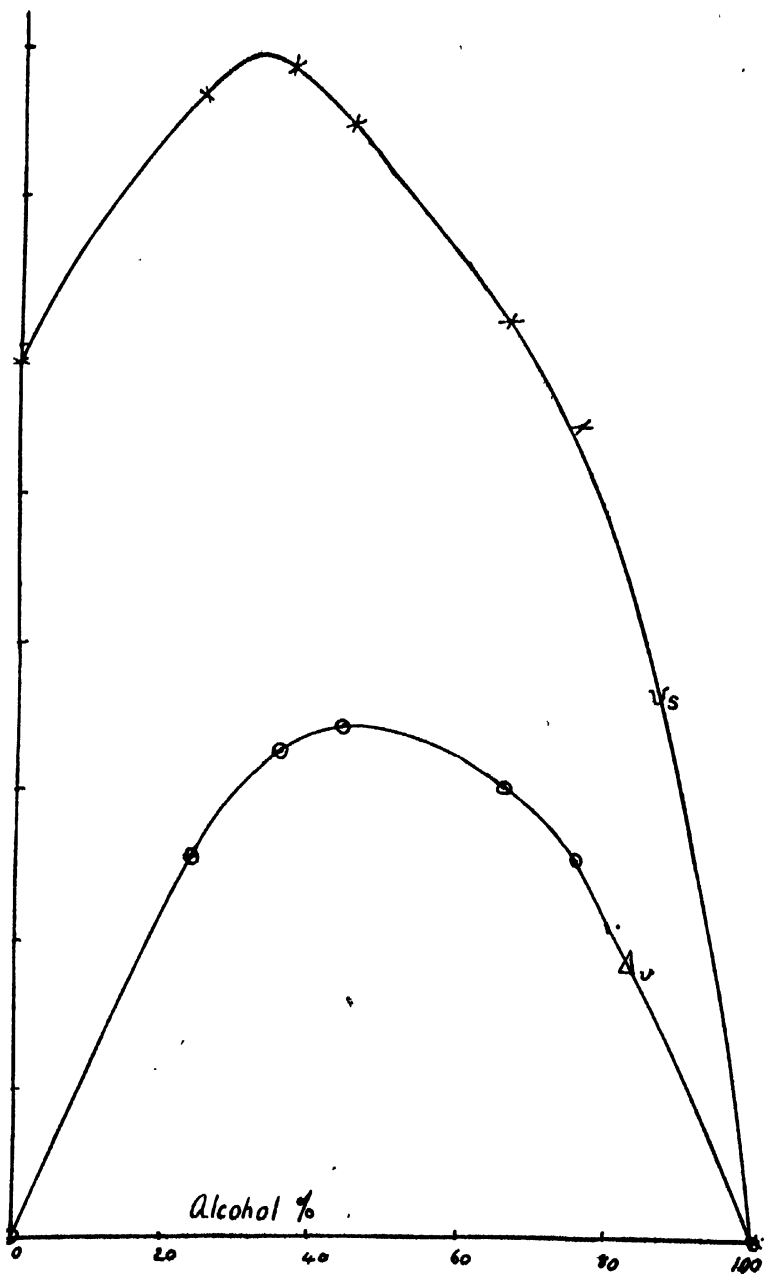| Alcohol per cent. in solvent.	Δ_v	v_s
0	...	·739
24·44	·0255	·757
35·70	·0326	·759
44·17	·0345	·755
66·13	·0305	·742
75·50	·0258	·735
100·00	...	·680

Fig. 2. Carbamide in Water-Alcohol Mixtures.

If the values of v_s be plotted against the composition of the solvent, a maximum value is found for a solution containing 32 per cent. alcohol (Fig. 2). The maximum value of Δ_v corresponds to about 44 per cent. alcohol. A similar series of results was obtained for solutions of carbamide at 30° C.

Table XXI.

Solute—Carbamide.   Temp. 30° C.

(a) In water (d_0 = ·995677).

A	d_1	v_s
2·3290	1·001575	·744
9·0567	1·017457	·745
15·4282	1·030922	·747

(b) In ethyl alcohol (d_0 = ·780777).

2·3698	·789391	·677
4·3264	·796280	·679

(c) In water-alcohol (25·44 per cent. alcohol).
d_0 = ·955387 Δ_v = ·0260 cc.

4·0276	·965613	·760
11·5191	·983142	·761

(d) In water-alcohol (30·47 per cent. alcohol).
d_0 = ·946572 Δ_v = ·0295 cc.

4·3638	·957766	·761
9·3135	·969667	·761

(e) In water-alcohol (36·62 per cent. alcohol).
d_0 = ·934695 Δ_v = ·0323 cc.

3·2901	·943409	·760
6·4193	·951311	·760
13·0705	·966975	·761

(f) In water alcohol (47·11 per cent. alcohol).
d_0 = ·912305 Δ_v = ·0339 cc.

4·5592	·924928	·752
7·7650	·933190	·756

(g) In water-alcohol (58·89 per cent. alcohol).
d_0 = ·885436 Δ_v = ·0323 cc.

5·2383	·900608	·747
13·2060	·921661	·749

If the values of v_s be compared for the concentration $A = 4$ the results are seen to vary in the same manner as those in Table XX.

Table XXII.

Alcohol per cent. in solvent.	Δ_v	v_s
0	...	·744
25·44	·0260	·760
30·47	·0295	·761
36·62	·0323	·760
47·11	·0339	·752
58·89	·0323	·747
100·00	...	·679

Results obtained with other solutes are given in the following tables.

Table XXIII.

Solute—Formamide.　Temp. 30° C.

(a) In ethyl alcohol ($d_0 = $ ·780777).

A	d_1	v_s
1·8454	·785604	·847
6·1292	·796280	·849
18·5815	·823708	·855

(b) In water-alcohol (44 per cent. alcohol) $d_0 = $ ·918665.

1·7433	·921389	·901
3·2160	·923652	·900
4·0509	·924849	·902

The corresponding determinations in aqueous solutions at 30° C. were not made since a complete series of values had already been obtained at both 20° and 25° C. The values of v_s for concentrations corresponding to the above are here given for these temperatures, and the values for 30° calculated by assuming that the difference in solution volume for 5° C. is the same between 30° and 25° as it is between 25° and 20° C.

(c) In water.

A	v_s 20° C.	v_s 25° C.	v_s 30° C.
1·7251	·847	·856	·865
4·2770	·848	·856	·865
17·2736	·854	·860	·866

The specific volume of liquid formamide at 30° C. was found to be ·88776, so that whereas the process of solution in either water or alcohol is accompanied by contraction, when dissolved in the mixture there is an increase in the volume of the system.

Table XXIV.

Solute—Acetamide.   Temp. 30° C.

(a) In water.

A	d_1	v_s
4·5875	·998254	·945
7·5278	·999892	·944
10·1471	1·001300	·943
16·7179	1·004590	·942

(b) In ethyl alcohol.

4·3441	·789723	·932
7·0327	·794941	·933
9·6461	·799847	·934

(c) In water-alcohol (25·44 per cent. alcohol).

5·3795	·959944	·949
13·2547	·965848	·950

(d) In water-alcohol (36·62 per cent. alcohol).

5·2768	·939815	·954
10·9203	·944726	·954

(e) In water-alcohol (47·11 per cent. alcohol).

4·5536	·917524	·953
9·5581	·922779	·954
16·2709	·929080	·955

(f) In water-alcohol (58·89 per cent. alcohol).

4·8831	·892021	·950
12·1520	·900599	·954

The specific volume of liquid acetamide, extrapolated for a temperature of 30° is ·956 (Meldrum and Turner),[1] and the values of v_s in solutions containing 36·62 and 47·11 per cent. alcohol are almost identical with this.

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[1] J.C.S., 1908, 93, 876.

Table XXV.

Solute—Propionamide.   Temp. 30° C.

(a) In water.

A	d_1	v_s
1·8533	·996096	·981
3·9972	·996593	·980

(b) In ethyl alcohol.

3·2024	·786515	·980
7·5389	·793896	·979
11·4767	·799920	·983

(c) In water-alcohol (47·11 per cent. alcohol).

4·9714	·916309	·995

The specific volume of liquid propionamide for this temperature is a 1·000.

Table XXVI.

Solute—Sucrose.   Temp. 30° C.

(a) In water.

A	d_1	r_s
2·7695	1·006078	·619
4·5190	1·012373	·621
8·2459	1·025524	·621

(b) In water-alcohol (25·44 per cent. alcohol).

5·9306	·977454	·625
9·5612	·990192	·625

(c) In water-alcohol (30·47 per cent. alcohol).

5·1754	·966014	·624
8·5266	·977847	·626

(d) In water-alcohol (36·62 per cent. alcohol).

6·8290	·960193	·625
8·9480	·967624	·627

(e) In water alcohol (47·11 per cent. alcohol).

4·8789	·930920	·625
10·9941	·952719	·627

(f) In water-alcohol (58·89 per cent. alcohol).

4·6037	·903305	·622
9·9049	·922626	·624

It will be seen from the above results that in every case considered, the specific solution volume of a solute is greater in a water-alcohol mixture than in either water or alcohol, and not intermediate between its value in the simple liquids.   In the case of formamide as solute the specific solution volume is actually greater than the specific volume of the pure liquid, although the solution volume in either water or alcohol is considerably less.   In the examples where the solution volume has been determined in a series of water-alcohol mixtures, a more or less definite maximum has been found, but the position of the maximum varies with the solute.   The maximum solution volume of carbamide is found in a solution containing about 32 per cent. of alcohol both at 25° and 30° C., but in the case of both acetamide and sucrose, the mixture corresponding to the maximum contains over 40 per cent. of alcohol.

Maxima or minima have been recorded for several physical properties of alcohol-water mixtures, but the position of such maxima are by no means constant.   These abrupt changes in the physical properties of mixtures have been interpreted by various authors as indicating combination between the alcohol and water with the formation of more or less stable "solvates."   If this be so, the results obtained for solution volumes of solutes in such mixtures indicate in addition, the existence in the solution of solvates between the solute and either water or alcohol or both.   The formation of a solvate results in a change in the specific volume, the magnitude of which will vary with the particular solvate in question.   Combination between the alcohol and water molecules results in a contraction in volume, which varies with the composition of the mixture and also the temperature.   If in such a mixture we dissolve a solute, which also forms a solvate with water (or alcohol) the original equilibrium of the system will be

altered, and a further volume change result. This second change may be in the same direction as the first or it may be in the opposite direction, depending on the relative magnitudes of the specific contraction accompanying the formation of solvate in each case.

In order to explain the results obtained in this work we would therefore have to consider that the formation of solvates is characteristic of all the substances that have been used as solutes. It is considered that the results obtained in this research can be explained by assuming that the observed volume changes result from a rearrangement of the molecules in the system.

From a consideration of the specific solution volumes of organic solutes in organic solvents Tyrer (loc. cit.) concluded "that a connection exists between the compressibility of a solvent, and the volume which a solute, when dissolved in it, takes up." In the case of solutions in water alcohol mixtures there is undoubtedly some connection between the specific contraction that has already taken place in the preparation of the mixture and the specific volume of a solute in this mixture.

The contraction which results from the mixing of water and alcohol is due to a condensation in the volume of the system resulting from a rearrangement of the molecules in such a way as to permit of closer packing. For any two liquids (e.g., alcohol and water) this condensation will tend towards a maximum corresponding to a certain mixture at any particular temperature. The effect of dissolving a solute in such a mixture will depend on the relative size of the molecule of solute, and the amount of condensation that has already taken place in the preparation of the solvent. In the case of the pure solvents (water or alcohol) the addition of solute will cause a rearrangement of molecules in the system resulting in a relatively large decrease

in total volume. In the case of a mixture of alcohol and water which is already condensed, the addition of the solute would be expected to have a smaller effect. The observed value of v^s would therefore be greater in such a mixture than in either of the simple solvents.

It follows from the results given above that the maximum solution volume of a solute is not always found in the mixture which has undergone the maximum contraction in its preparation. Thus in the case of carbamide, the maximum solution volume occurs in a 32 per cent. alcohol mixture, whereas the maximum specific contraction (between water and alcohol) takes place when the mixture contains about 44 per cent. alcohol. The position of the observed maximum contraction depends on the relative volumes of the different molecules concerned.

On the HYDROLYSIS of UREA HYDROCHLORIDE.

By George Joseph Burrows, B.Sc.

ON THE HYDROLYSIS OF UREA HYDROCHLORIDE.

By George Joseph Burrows, B.Sc.

THE hydrolysis of urea hydrochloride in aqueous solutions has been investigated by Walker[1] and Walker and Wood.[2] These authors found that the salt was hydrolysed by water into urea and free hydrochloric acid, the amount so hydrolysed at any dilution being expressed by the equation

$$K = \frac{h^2}{(1-h)v}$$

where h is the fraction of salt hydrolysed

v is the volume in litres containing 1 gram molecule of the salt (total)

and K is the equilibrium constant.

The results contained in the present paper were obtained during an investigation of the properties of water-alcohol and water-acetone mixtures. In such mixtures the total amount of water present can be decreased considerably without altering the total volume of the solution, and it appeared of interest to see how such a change in the nature of the solution would affect the degree of hydrolytic dissociation of urea hydrochloride. It has been found that in these mixtures the equilibrium between hydrolysed and unhydrolysed urea hydrochloride can also be expressed in terms of Ostwald's dilution law for electrolytic dissociation. Some of the results included in this paper were published in a previous paper on the rate of decomposition of urea in

Zeit. physik. Chem. IV, 319.   [2] J.C.S., 1903, 83, 484.

water-alcohol mixtures.[1] The investigation has since been
extended, the degree of hydrolysis of urea hydrochloride of
different concentrations having been determined in mixtures
of water and ethyl alcohol and water and acetone.

I. Ethyl alcohol-water Mixtures.

The method employed for determining the degree of
hydrolysis of the hydrochloride was similar to that described
by Walker *(loc. cit.)* for aqueous solutions, and is as follows.
The rate of inversion of sucrose solution by hydrochloric
acid was determined, and then the rate of inversion by
hydrochloric acid containing the required amount of urea.
By assuming that the rate of inversion of the sucrose is
proportional to the concentration of free acid (for any par-
ticular solvent), the degree of hydrolysis of the salt is
expressed as the ratio of the inversion velocity in the solu-
tion containing urea to that in the solution containing no
urea. The method adopted in preparing the solutions and in
following the course of the reaction was the same as that
described in a previous paper on sucrose inversion.[2]   All
alcohol or acetone percentages given in this paper are by
volume.

The rate of inversion was calculated from the usual
equation

$$k = \frac{1}{t} \ \log_{10} \frac{R_0 - R_\infty}{R_t - R_\alpha}$$

Where R_0 is the initial rotation

R_∞ is the rotation after complete inversion

R_t is the rotation after an interval of t minutes.

The agreement between the values of k obtained in any
experiment was quite satisfactory. The following table
contains the result of an experiment with 70 per cent.
alcohol as the solvent and is quoted as an example.

[1] Burrows and Fawsitt, J.C.S., 1914, 105, 612.

[2] J.C.S., 1914, 105, 1260.

Table I.

10 per cent. sucrose, N/2 hydrochloric acid and M/2 urea in 70 per cent. alcohol. Temperature 25° C.

t	R_t	k
0	58·0	...
30	53·3	·00100
50	50·2	·00102
70	47·5	·00100
100	43·0	·00104
138	37·8	·00106
180	33·4	·00104
210	30·4	·00103
240	27·5	·00103
270	24·8	·00103
288	23·5	·00102
∞	– 12·2	...
		mean ·00103

In Table II are given under k_1 the mean values obtained for the rate of inversion of 10 per cent. sucrose by N/2 hydrochloric acid. Under k_2 the rate of inversion by M/2 urea hydrochloride and under $\dfrac{k_2}{k_1}$ the ratio for the different water-alcohol mixtures at 25° C.

Table II.

Alcohol % (vol.)	k_1	k_2	$\dfrac{k_2}{k_1}$
0	·00219	·00143	·653
40	·00192	·00112	·583
50	·00177	·00103	·579
60	·00185	·00101	·543
70	·00200	·00103	·515

The ratio $\dfrac{k_2}{k_1}$ does not represent the true degree of hydrolysis of the urea hydrochloride. As pointed out by Walker and Wood (loc. cit.), the inversion velocity is influenced by the presence of unhydrolysed salt. The latter affects the

degree of dissociation of the free hydrochloric acid and it
also has a direct effect on the rate of inversion of the
sucrose. To correct for this, Walker and Wood determined
the effect on the rate of inversion caused by the addition
of an amount of sodium chloride equal to that of the
unhydrolysed urea hydrochloride, and assumed that this
gave approximately the effect of the unhydrolysed salt on
the reaction. In a similar manner the present author has
determined the rate of inversion by $N/2$ (HCl + NaCl) in
alcoholic solutions. Thus, a solution in 50 per cent. alcohol
which was seminormal with regard to the total chlorine,
but contained 57·9 per cent. of this as hydrochloric acid
and 42·1 per cent. as sodium chloride, was found to give a
mean rate of inversion of sucrose $k = ·00092$. As the
corresponding value for the inversion by $N/2$ hydrochloric
acid and $M/2$ urea was ·00103 the correct degree of hydro-
lysis is considered to be $·579 \times \dfrac{103}{92}$. The correcting
factor was determined in a similar way for each of the
other solutions.

In Table III are given the values for the degree of hydro-
lysis (h) corrected in this way.

Table III.

M/2 urea hydrochloride.   Temperature 25·0° C.

Alcohol % (vol.)	$\dfrac{k_2}{k_1}$	factor	h
0	·653	1·059	·691
40	·583	1·100	·647
50	·579	1·120	·648 [·630]
60	·543	1·110	·603
70	·515	1·107	·570

The degree of hydrolysis is seen to decrease with decreas-
ing concentration of water. The value for 50 per cent.
alcohol is obviously too high. The value for this solution,
obtained by plotting a curve for the other mixtures, is $h =$

·630; this value will be used in the subsequent discussion. Experiments were also performed with solutions containing N/2 hydrochloric acid and M/2 urea at 30° C. It was found that at this temperature the value for h in water was the same as at 25° C., while the value in 70 per cent. alcohol was decreased by about 3 per cent. From the figures in Table III it is possible to calculate the hydrolysis constant for urea hydrochloride in each of these mixtures. If we represent the degree of hydrolysis by h, and the volume in litres which contains 1 gram molecule of urea hydrochloride by v, (which in this case equals 2) then the hydrolysis constant H is given by

$$H = \frac{h^2}{(1 - h)v}$$

The values of H are given in Table IV.

Table IV.

Alcohol % (vol.)	h	H
0	·691	·773
40	·647	·593
50	·630	·536
60	·603	·458
70	·570	·378

The value of H in water is a little lower than that given by Walker and Wood (·781). This is due to the small differ- ence between the values of h found by them and the present author.

The degree of hydrolysis of M/10 urea hydrochloride was determined at 40° C. These results are given under h_1 in Table V, together with the values calculated from H under h (calc). In determining h_1 no correction has been applied to the ratio $\frac{k_2}{k_1}$ as it has been considered unnecessary owing to the small effect of the unhydrolysed salt at this com- paratively high dilution. The values under h (calc) are

calculated from the corresponding values of H (at 25° C.) by substituting in the equation

$$H = \frac{C_A \times C_B}{C_{AB}}$$

where C_A = the concentration of free hydrochloric acid

C_B = the concentration of free urea

C_{AB} = the concentration of unhydrolysed salt

Table V.

Alcohol % (vol.)	k_1	k_2	h_1	h (calc.)
0	·00265	·00241	·906	·897
25	·00255	·00219	·859	·882
50	·00230	·00196	·852	·860
75	·00274	·00219	·800	·805

Experiments with 10 per cent. sucrose and N/2 hydrochloric acid and M/4 urea at 25° C. gave the following results.

Table VI.

Alcohol % (vol.)	k_1	k_2	factor	h_1	h (calc.)
0	·00219	·00172	1·03	·809	·826
25	·00204	·00154	1·05	·793	·811
75	·00208	·00143	1·06	·729	·737

The agreement between the calculated and experimental results justifies the conclusion that in water-alcohol mixtures the effect of dilution may be expressed by the ordinary dilution law. That is, the amount of salt hydrolysed depends on the concentration of the salt expressed in terms of the total volume—it is not simply proportional to the amount of water in the solution.

II. Acetone-water Mixtures.

Similar experiments were carried out with acetone-water mixtures as solvents. In this case the concentration of free acid was determined by its effect in hydrolysing methyl acetate. In determining the degree of hydrolysis of the

urea hydrochloride, the rate of hydrolysis of methyl acetate was determined, first in a solution containing hydrochloric acid, and then in a solution containing urea hydrochloride. The rate of hydrolysis of methyl acetate was calculated from the equation

$$k = \frac{1}{t\sqrt{4\,a\,n+1}}\ \log\frac{4\,a\,n + 2\,n\,x\,(\sqrt{4\,a\,n+1}-1)}{4\,a\,n - 2\,n\,x\,(\sqrt{4\,a\,n+1}+1)}$$

obtained by integrating $\dfrac{d\,x}{d\,t} = k\,(a-x) - k_1\,x^2$

where k = the rate of hydrolysis

k_1 = the rate of esterification

a = the initial concentration of ester

x = amount of ester hydrolysed in time t (minutes)

$n = \dfrac{a-\xi}{\xi^2}$.

and ξ = amount of ester hydrolysed from the beginning of the reaction up to the equilibrium. The value of x was found by determining the amount of acetic acid in the solution after different intervals of time by titrating a portion with baryta solution.

The values of k found in any experiment were constant to within about 2 per cent. of the mean. An example is given in detail in Table VII for the rate of hydrolysis of 5 per cent. methyl acetate by N/2 hydrochloric acid and M/2 urea in water at 25° C.

Table VII.

t	x	$k \times 10^4$
0	...	...
30	·0600	9·14
60	·1192	9·20
91	·1733	9·09
120	·2250	9·23
150	·2692	9·10
212	·3600	9·19
270	·4275	9 03
332	·4975	9·10
		Mean 9·13

In Table VIII are given the mean results obtained for the rates of hydrolysis of 5 per cent. methyl acetate in acetone-water mixtures at 25° C.

In this table k_1 is the rate of hydrolysis by N/2 hydrochloric acid, and k_2 is the rate of hydrolysis by M/2 urea hydrochloride.

Table VIII.

Acetone % (vol.)	$k_1 \times 10^4$	$k_2 \times 10^4$	$\dfrac{k_2}{k_1}$
0	13·58	9·13	·672
20	12·28	7·98	·650
40	10·33	6·02	·583
60	7·91	3·91	·494
80	7·51	2·27	·303

As in the case of sucrose inversion the effect of unhydrolysed salt was determined, by finding in each of the above mixtures the rate of hydrolysis by N/2 (HCl + NaCl), the amount of sodium chloride taken in each case being the approximate amount of unhydrolysed urea hydrochloride found above. The ratio of this number to the corresponding value of k_2 is taken as the correcting factor for each solution, and by multiplying $\dfrac{k_2}{k_1}$ by this factor the value of h, the degree of hydrolysis, is obtained. These results are given in Table IX. Under H are given the values of the hydrolysis constants of urea hydrochloride calculated from the equation $H = \dfrac{h^2}{(1-h)\,v}$ where v is the volume in litres containing one gram molecule of urea hydrochloride and in this case equals 2.

Table IX.

Acetone % (vol)	$\dfrac{k_2}{k_1}$	factor	h	H
0	·672	1·03	·692	·777
20	·650	1·04	·676	·705
40	·583	1·06	·618	·505
60	·494	1·06	·523	·285
80	·303	1·08	·328	·080

The hydrolysis constant decreases considerably as water is replaced by acetone, the effect being greater than when water is replaced by alcohol. The degree of hydrolysis of M/10 urea hydrochloride at 25° C. was also determined in each of these mixtures. The results are given in Table X. k_1 is the rate of hydrolysis of 2·5 per cent. methyl acetate by N/10 hydrochloric acid. k_2 is the rate of hydrolysis of 2·5 per cent. methyl acetate by M/10 urea hydochloride.

$$h = \frac{k_2}{k_1} = \text{degree of hydrolysis.}$$

On account of the small amount of unhydrolysed urea hydrochloride in these solutions the ratio $\frac{k_2}{k_1}$ has not been corrected as in the more concentrated solutions.

Under h (calc.) are given the values for the degree of hydrolysis of M/10 urea hydrochloride calculated from the hydrolysis constants H, given in Table IX.

Table X.

Acetone % (vol)	$k_1 \times 10^4$	$k_2 \times 10^4$	h	h (calc.)
0	2·60	2·32	·893	·895
20	2·39	2·10	·879	·885
40	1·90	1·64	·863	·855
60	1·42	1·15	·810	·785
80	1·13	0·725	·642	·580

The agreement between the calculated and experimental values of h is satisfactory in all cases except in the mixture containing 80 per cent. acetone. On account of the small value of h for M/2 urea hydrochloride in this mixture, a small error in this determination would produce a relatively large error in H, and on this account there is more likelihood of a difference between the calculated and experimental values of h for M/10 urea hydrochloride in this solution than in the others.

In the next series of experiments the solvent was kept constant (60 per cent. acetone) and the concentration of

the urea hydrochloride varied. In Table XI are given the results for the degree of hydrolysis of urea hydrochloride of various concentrations in this particular mixture at 25°C. The values under h (calc.) were obtained from $H = \cdot315$, which in turn was calculated from the value $h = \cdot810$ found for M/10 urea hydrochloride.

Table XI.

Concentration of urea hydrochloride	$k_1 \times 10^4$	$k_2 \times 10^4$	$\dfrac{k_2}{k_1}$	factor	h	h (ca'c)
M/2	7·91	3·91	·494	1·06	·523	·554
M/4	3·60	2 39	·664	1·03	·684	·675
M/6	2·38	1·81	·760	1·01	·767	·737
M/8	1·77	1·39	·785	...	·785	·780
M/10	1·42	1·15	·810	...	·810	[·810]
M/16	0·870	0·749	·861	...	·861	·865
M/32	0·438	0·406	·927	...	·927	·925

The agreement between the calculated and experimental values of h is considered satisfactory.

A comparison of the figures given in Tables IV and IX shows that the degree of hydrolysis is not independent of the nature of the substance which replaces the water as solvent. Whereas the value of h in aqueous solution is ·691, in 60 per cent. alcohol it is ·603, and in 60 per cent. acetone only ·523. In the case of alcohol-water mixtures the hydrolysis constant H is (approximately) proportional to the total number of molecules of water + alcohol. This is shown in Table XII, in which w represents the number of gram molecules of water in the solution, and a the number of gram molecules of alcohol.

Table XII.

Alcohol % (vol.)	a	w	$(a+w)$	H	$\dfrac{H \times 10^2}{w}$	$\dfrac{H \times 10^2}{w+a}$
0	0	50·0	50·0	·773	1·54	1·54
40	6·25	30·5	36·75	·593	1·94	1·61
50	7·83	25·5	33·33	·536	2·10	1·61
60	9·22	20·0	29·22	·458	2·29	1·57
70	10·75	15·0	25·75	·378	2·52	1·47

In the case of acetone-water mixtures the value of H is approximately proportional to the number of molecules of water in the solution, the acetone apparently having no hydrolytic effect.

Table XIII.

Acetone % (vol.)	w	H	$\dfrac{H \times 10^2}{w}$
0	51·0	·777	1·52
20	41·0	·705	1·76
40	31·0	·505	1·63
60	20·0	·285	1·43
80	9·0	·080	0·89

These results indicate that in the mixtures investigated, whereas the hydrolytic power of alcohol is approximately the same as that of water, acetone appears to have no effect on the degree of hydrolysis of urea hydrochloride.

CINEOL AS A SOLVENT IN CRYOSCOPY.

CINEOL AS A SOLVENT IN CRYOSCOPY.

By CHARLES E. FAWSITT and CHRISTIAN H. FISCHER.

[*Read before the Royal Society of N. S. Wales, December 5, 1917.*]

CINEOL is an important constituent of many Eucalyptus oils and it is now easily procurable in a fairly pure condition. Its composition is given by the formula $C_{10}H_{18}O$. It was thought that its value as a possible solvent for cryoscopic determinations was worth investigation.

The cineol was obtained from Hudson's Eumenthol Co., Sydney, where, we understand, it is obtained from eucalyptus oil, which is rich in cineol. The cineol is obtained from the oil by freezing out this constituent. We distilled the cineol and found that most of it came over at $175°$ – $176°$ C. The freezing point of the distilled cineol was $0·1°$ C. The figure usually given for the freezing point of cineol is $-1°$C., but this latter figure is too low.

Pure cineol is exceedingly hygroscopic, and owing to the relatively small molecular weight of water, small amounts of absorbed water depress the freezing point very much. An addition of $0·2\%$ of water was found to depress the freezing point of cineol $0·54°$ C.

In order to test whether the distilled cineol had any considerable amount of moisture in it, a current of air, dried by sulphuric acid, was passed through the solution for three quarters of an hour, when the freezing point rose to $0·2°$ C. Some distilled cineol was next allowed to stand over sodium for twenty-four hours and redistilled; its freezing point was found to be $0·9°$ C.

Cineol as a Solvent in Cryoscopy.

For the first determinations given below, distilled cineol of F.P. $0·1°$ C. was used. This contained a small quantity

of water but was easier to work with than the purer cineol
of F.P. 0·9° O. used in the later determinations.

Tho use in cryoscopy of a solvent containing slight im-
purities is justified if the depressions of the freezing point
caused by additions of various solutes are the same as they
would have given with the purer solvent. Whether this is
so, is a matter for experiment in any particular case.

We have found that when benzene is used as a solute,
exactly the same results were obtained with the ordinary
and the dried cineol, and we believe that the influence of
this small quantity of moisture is negligible for its use in
the determinations given below.

The usual apparatus with a Beckmann thermometer was
used for these determinations, except that the stirrer was
fitted with a mercury seal, in order to exclude air with its
attendant moisture. Without this, or other suitable con-
trivance for preventing moisture from entering, it is
impossible to obtain results that can be depended on.

After the freezing point had been registered in any par-
ticular determination, the tube containing the solvent and
solute was warmed up to nearly the room temperature (16°
−23° O.) before refreezing to obtain another reading. This
method gave better results than heating the semifrozen
liquid just sufficiently high to melt all solid.

In the following tables "K," the cryoscopic constant, is
the depression in the freezing point caused by dissolving
one gramme-molecule of the solute in 1000 grammes of
cineol.

"K" is calculated from the formula

$$K = \frac{m \times \triangle \times W}{w \times 1000}$$

Where m = molecular weight of the solute.

$\triangle$ = depression of the freezing point in degrees
centigrade.

w = weight of solute used (in grammes).

W = weight of solvent used (in grammes).

The solutes used were Kahlbaum's in the case of benzophenone, nitrobenzene, bromobenzene, toluene, benzene, butyl alcohol, and were used without further purification. The chloroform used was Mercks'. The ethyl alcohol used was Mercks', and was distilled after being in contact with quicklime for twenty-four hours. The ether was Kahlbaum's and was distilled after being in contact with sodium for twenty-four hours.

TABLE I.

Solute:—Benzophenone $(C_6H_5)_2CO$; m = 182.

Weight of solvent (cineol) = 14·258 grammes.

	Percentage of solute to solvent.		K. (calculated)
0·1186	0·832	0·308	6·7
0·2026	1·421	0·532	6·8
0·2752	1·930	0·696	6·6
0·3870	2·714	1·044	7·0
			Average 6·75

TABLE II.

Solute:—Nitrobenzene, $C_6H_5NO_2$; m = 123.

Weight of cineol = 16·06.

w.	Percentage of solute.	$\triangle$	K. (calculated)
0·2054	1·279	0·655	6·4
0·2946	1·834	0·953	6·4
0·5068	3·156	1·651	6·4
0·6572	4·092	2·176	6·6
			Average 6·45

TABLE III.

Solute:—Bromobenzene, C_6H_5Br; m = 157. W = 16·02.

w.	Percentage of solute.	$\triangle$	K.
0·197	1·23	0·54	6·9
0·3444	2·15	0·949	6·9
0·4872	3·04	1·317	6·8
0·6386	3·98	1·703	6·7
			Average 6·8

TABLE IV.

Solute:—Toluene, $C_6H_5CH_3$; $m = 92$. $W = 24.69$.

w.	Percentage of solute.	$\triangle$	K.
0·203	0·822	0·599	6·7
0·403	1·63	1·199	6·8
0·613	2·48	1·814	6·7
0·849	3·44	2·508	6·7
			Average 6·7.

TABLE V.

Solute :—Benzene, C_6H_6; $m = 78$. $W = 20.31$.

w.	Percentage of solute.	$\triangle$	K.
0·1902	0·937	0·788	6·6
0·3452	1·70	1·428	6·6
0·5220	2·57	2·155	6·5
0·8422	4·15	3·428	6·4
			Average 6·5

TABLE VI.

Solute :—Chloroform, $CHCl_3$; $m = 119.4$. $W = 19.19$.

w.	Percentage of solute.	Δ	K.
0·22	1·146	0·639	6·7
0·4136	2·156	1·20	6·7
			Average 6·7

TABLE VII.

Solute :— Ethyl ether, $(C_2H_5)_2O$; $m = 74$. $W = 18.27$.

w.	Percentage of solute.	Δ	K.
0·1292	0·707	0·624	6·5
0·2698	1·477	1·275	6·4
0·4016	2·2	1·875	6·3
0·6210	3·4	2·875	6·3
0.94	5·15	4·255	6·1
			Average 6·3.

From these results the value of the constant (K) may be taken as 6·7. This holds good for dilute solutions and for unassociated solutes.

Cineol itself does not appear to show any abnormal behaviour in these experiments, and molecular weight determinations of cineol (as solute) dissolved in benzene (solvent), gave a normal result for the molecular weight of cineol. The values of the constant "K" for cineol in some of the tables given above decrease with increasing concentration of solute, but this is a peculiarity often noticed in such freezing point experiments, and it may be taken that the more correct value for the constant is that obtained in the dilute solutions.

The molecular weight of substances containing the group hydroxyl, would be expected to be abnormal (too large) in solution in cineol, as this abnormal character of such solutes is noticed with other solvents. *Vice versa*, the calculated values of "K" using the normal molecular weights for alcohols should come out rather low.

TABLE VIII.

Solute:—Ethyl alcohol, C_2H_6 46. $W = 16·90$.

$w.$	Percentages of solute.		$K.$
0·1478	0·875	1·113	5·8
0·3834	2·27	2·645	5·4
0·6934	4·105	4·356	4·9

TABLE IX.

Solute:—Butyl alcohol, $C_4H_{10}O$; $m = 74$. $W = 18·02$.

$w.$	Percentages of solute.	Δ	K
0·132	0·732	0·60	6·1
0·398	2·21	1·744	5·8
0·691	3·84	2·877	5·5

From these results we conclude that these alcohols are associated in solution in cineol. Comparing cineol with other solvents, we find it is somewhat more difficult to carry out determinations with cineol as solvent, than with benzene or water, but we believe that cineol will be found a useful solvent in some cases.

The latent heat of fusion for cineol is given by the formula

$$L = \frac{RT^2}{K \times 1000}$$

where L = latent heat of fusion of 1 gramme of cineol, R = 1·985, and T = absolute temperature of melting point of cineol = 274° C. The latent heat of cineol (1 gramme) is therefore 22·2.

Summary.

1. Cineol is a hygroscopic substance and the usual freezing point given is too low. Cineol purified from dissolved water was found to freeze at 0·9° C.

2. The freezing point constant for normal solutes in cineol as solvent is 6·7.

BEHAVIOUR OF IRON IN CONTACT WITH
SULPHURIC ACID.

EXPERIMENTS ON THE BEHAVIOUR OF IRON IN CONTACT WITH SULPHURIC ACID.

By C. E. FAWSITT, D.Sc, and A. A. PAIN, B.Sc.,

Two papers on this subject have already appeared.[1] Comparatively little research on this subject has been carried out, yet the matter is of great importance; the researches already published (*loc. cit.*) have therefore been continued. There are many peculiarities about the action of sulphuric acid on iron that have still to be cleared up, but we have confined our present experiments to two questions only.

Part I.—*A comparison of Iron in concentrated Sulphuric Acid with Passive Iron.*

Although iron is attacked very noticeably when first inserted into concentrated sulphuric acid, the action is much less vigorous after a few hours, and suggestions have been made by some chemists to us that in this case we may have to do with something resembling a "*passive*" state of iron. We have therefore performed some experi-

[1] Fawsitt and Powell, *Journ. Soc. Chem. Ind.*, xxxiii, 284, 1914; and Powell, *Proc. Roy. Soc. N.S.W.*, xlvii, 59, 1913.

ments with wrought iron and 96% sulphuric acid (pure for
analysis).

If the word "*passive*" be here used as denoting "*inac-
tive*," then there is no great objection to it, for the activity
in the case of action on wrought iron and cast iron is
excessively slight.   But the word "passive" could not at
any rate be applied to iron in pure sulphuric acid as denoting
a state in any sense similar to that of the state of iron when
placed in 1·4 sp. gr. nitric acid.   The results of the follow-
ing experiments bring out the difference between the two
cases.

I.—I A. When passive iron, lying in 1·2 nitric acid was
    touched with platinum, neither iron, nor the platinum
    experienced any change noticeable to the eye.

  I B. When iron lying in concentrated sulphuric acid (96%)
    was touched with platinum, then although there might
    have previously been no bubbles of gas coming from
    the iron, bubbles of gas appeared after contact almost
    immediately on the platinum.

II.—II A. The cell. Passive iron [1·2 nitric acid] Platinum
    was found to have a potential of 0·13 to 0·3 volt, while
    the cell Active Iron [1·2 nitric acid] Platinum had a
    potential of 0·95 to 1·1 volts.   In both cases the iron
    was positive to the platinum.

When passive iron immersed in 1·2 nitric acid was touched
with tin or copper, the iron became suddenly active, and
the potential immediately rose to that of the second cell,
viz., 1·1 volts.   When the passive iron was lifted into the
air for a few moments and replaced in the solution, there
was no considerable influence on the potential of the cell.

  II B. The E.M.F. of the cell.   Iron [concentrated sul-
    phuric acid] Platinum was found to be much more
    variable than the E.M.F. of the cell where iron, passive

or active, is tested against platinum in nitric acid. This is shown in Table I.

Table I.

Time after contact of iron with acid.	Potential
1 Minute	1 · 2 volts
8 ,,	1 · 1 ,,
16 ,,	0 · 95 ,,
30 ,,	0 · 8 ,,
65 ,,	0 · 62 ,,

After 65 minutes insertion in the acid, the iron was touched with a piece of tin, when the potential rose only to 0·68 volts. The iron was then scratched vigorously with tin, when the potential rose to 0·79 volts. The potential however started to fall again immediately. On bringing the iron now into the air for one minute, and again introducing into the sulphuric acid, the potential was found to have risen to 0·95 volt. The voltage immediately began to decrease slowly again as before. Whenever the iron was lifted into the air for one minute, the potential rose considerably, and in some cases as much as 0·4 volt.

III.—Passive iron (made passive by 1·4 sp. gr. nitric acid) was put into concentrated sulphuric acid (96%).

In the concentrated sulphuric acid the potential of the cell —Passive Iron [concentrated sulphuric acid] Platinum— was found to be from 0 to 0·2 volt. When the passive iron was brought into the air for a minute, and then replaced in the sulphuric acid, the potential was not noticeably affected. On touching the passive iron (while in the sulphuric acid) with a piece of copper, the potential rose suddenly to 1 . 15 volts.

It will be seen from these experiments that wrought iron made passive by 1·4 nitric acid, bears no simple relation to ordinary (active) iron which has been lying in pure concentrated sulphuric acid for some time.

The slow action of concentrated sulphuric acid on iron or steel, whereby hydrogen is produced, is dependent on all the usual factors governing the action of acids on metals. The peculiarities noticed in the case of iron and concentrated sulphuric acid are due partly to the protective coating of $FeSO_4$, H_2O which tends to cover the iron soon after the action has begun; partly also, we think, to the fact that iron is capable of absorbing hydrogen; and partly to impurities in the iron. Concentrated sulphuric acid does not of itself passidify iron.

Part II.—*Variation in the rate of action according to the Concentration of Acid.*

It would probably be expected that dilution of the acid would greatly increase the velocity of action. Our experiments have shown, however, that the increase in action is not in any way proportional to the increase in the percentage of water in the acid, but rather that no great increase in the rate of action is obtained when the acid is reduced from 94 per cent. to a concentration of 85 per cent. H_2SO_4 (15% water). Below a concentration of 85% sulphuric acid, the velocity increases somewhat more noticeably as the concentration of H_2SO_4 diminishes. A further decidedly greater increase in velocity is noticed in proceeding from 70% acid to 64·5% acid. Some investigations into the rate of action of concentrated sulphuric acid on iron have been made by Knietsch.[1] Broadly speaking, it might be said that his experiments give somewhat similar results to those we have obtained.

An exceptionally slight action was obtained in our experiments with 89·3% H_2SO_4. Knietsch, on the other hand, obtained a minimum action with 94% H_2SO_4. This may possibly be accounted for by the different kind of iron used in the two researches.

[1] *Journ. Soc. Chem. Ind.*, xxi, p. 343, 1902.

The rather sudden increase in velocity of action which we have observed in proceedings from 85% to 80% and from 70% to 64·5% acid, may not be unconnected with the fact that the monohydrate, H_2SO_4, H_2O contains 84·5% of H_2SO_4 while the trihydrate H_2SO_4, $3 H_2O$ contains 64·7% H_2SO_4.

The amount of action depends to some extent on whether the acid is kept in movement or is left undisturbed in contact with the iron. One set of experiments, Series A, was conducted without shaking, and the rate measured by reading the volume of gas (reduced to N.T.P.) evolved from the iron and acid contained in a flask. In Series B, the flasks containing the iron and acid were shaken, and the rate measured by noting the diminution in weight of the iron used.

Series "A."

The iron used was a steel wire of the following composition:—carbon 0·51%, phosphorus 0·046%, silicon 0·083%, sulphur 0·058%, manganese 0·48%. The steel wire had a diameter of 0·0706 centimetres.

A length of 634 cm. of wire, weighing 20 grams, was polished with emery paper and was cut up into lengths of 5 cm. This lot of 20 grams weight was the amount used in each experiment, and the surface exposed to the acid was approximately 143 sq. cms. in each case. The volume of the acid used was 120 cc. This was put into a Jena distilling flask (130 cc.) with the portion of the neck above the side tube shortened so as to reduce the gas space in the flask to a minimum. The side tube was shaped to a delivery tube permitting the collection of evolved gas over mercury. After introducing the iron and acid, the neck of the flask was closed with a paraffined rubber stopper. This arrangement was proved to be gas-tight under a pressure of 24 cm. of mercury. The flasks were placed in a water

thermostat at 30° C., and the gas was collected in a measuring tube over mercury.

Owing to it being necessary to displace a small and variable amount of mercury in the delivery tube before any readings of the volume could be made, it was necessary to wait for 1 – 8 days, before the first reading could be taken. When therefore no reading for the volume of gas is given in the first few days (Table II), this does not mean that no gas was evolved, but that it was not possible to register the volume with the method of collection which was adopted.   Using 120 cc. of acid, there is not a very marked change in the concentration of the acid even in several weeks, for although acid is being used up by water it is also used up in order to form the compound $FeSO_4$, H_2O, which has been shown[1] to be the compound formed in the action of concentrated sulphuric acid on iron. $Fe + H_2SO_4 + H_2O$ $= FeSO_4, H_2O + H_2$.

An extreme case is next given where the action is taken as much greater than anything actually experienced in these experiments.   Taking 94% acid as an example, and allowing this to act on steel for 45 days at 30° C., the maximum amount of gas which could be produced in this time (30° C.) from 140 sq. cm. of the steel used, is say, 45 $\times$ 24 $\times$ 3·5 cc. = 3780 cc.   This (maximum) amount of gas is calculated on the assumption that the velocity throughout was the maximum velocity ever obtained in an experiment with 94% acid at 30° C.

These 3·780 litres would use up 16·8 grams of sulphuric acid (H_2SO_4).   16·8 grams of acid and 3·93 grams of water are thus removed.   Now the original acid had a volume of 120 cc. and weighed 217·4 grams; this contains 205·8 grams H_2SO_4 and 11·6 grams water.   After 45 days action 189 grams acid and 7·7 grams water are left, so that the per-

[1] Powell, *Proc. Roy. Soc. N.S.W*, XLVII, 59, 1913.

centage of H_2SO_4 in the acid is 96·08. A concentration
of 84·5% acid corresponds to the composition of the mono-
hydrate H_2SO_4, H_2O and so will not gain or lose in con-
centration when acting. More dilute acids will lose in
concentration.

As the acids employed usually had a much smaller action
in these experiments than that formulated in the calcula-
tion, any alteration in the concentration of the acid from
the initial values may be regarded as negligible.

In a previous research[1] it was suggested that the real
(maximum) velocity of the action of concentrated sulphuric
acid might not always be obtained owing to the adhering
coats of ferrous sulphate and other causes. In many of
those cases, shaking appears to be all that is necessary to
produce the maximum velocity.

In many of the experiments, the results of which are given
below, the velocity of action increased continually towards
the maximum as time advanced, even when the flasks were
not shaken; one could explain this by assuming that the
faster the evolution of hydrogen gas, the more stirring
action there is of the acid at the surface of the iron exposed;
or one could assume that the products of the action have
some accelerating effect on the action. It was assumed in
a previous research, using the same steel and 94·6% acid,
that the velocity of action obtained at 30° C. viz. 2·4 cc.
per sq. dcm. per hour, approximated pretty closely to the
the maximum velocity obtainable. In the first experiment
(Series A, Table II) the flasks were left quite undisturbed
except for the stirring action of the gas evolved, and the
velocities obtained with 94% acid were somewhat less than
those obtained originally by Fawsitt and Powell (loc. cit.)
with 94·6% acid. The concentration of acid in those solu-
tions was determined in the first instance by density, but

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[1] Journ. Chem. Soc. Ind., xxxiii, 284, 1914.

TABLE II.—Evolution of gas expressed in cubic centimetres at N.T.P. from 1 sq. decimetre per hour at 30°C.

Time from first contact	94% H₂SO₄	94°	90·9%	89·3°	89·3%	87·9%	87·9%	85%	85%	80°	80°	77·4°	77·4°	70%	70%	64·5%
¼ day	…	…	…	…	0·006	0·008	0·1	0·014	…	0·02	…	…	0·66	…	…	…
1 „	…	…	…	…	…	…	…	…	…	0·2	0·38	0·07	0·02	0·61	0·42	2·2
2 „	…	…	…	…	0·018	0·07	0·4	…	…	1·04	…	0·62	0·37	0·9	0·8	4·1
3 „	…	…	…	…	…	…	…	…	…	…	…	0·07	…	…	1·4	5·8
4 „	…	…	…	…	0·035	0·13	0·075	0·05	0·07	…	…	0·74	…	…	2·0	
5 „	…	…	…	…	…	0·155	0·12	0·12	0·11	2·6	2·0	1·7	…	1·4		
6 „	0·003	…	0·016	0·12	0·044	0·2	0·16	0·16	0·16	3·4	2·9	…	…			
7 „	0·005	…	0·17	…	0·053	0·26	…	0·21	0·20	…	3·5	2·9	…			
9 „	0·10	0·06	0·17	…	0·064	0·44	0·34	0·30	…	…	…	3·1	…	1·8		
11 „	…	0·17	…	…	…	…	0·36	0·46	0·38	4·9	2·6	3·4	…	2·0		
13 „	0·30	0·27	0·30	0·14	…	0·25	…	…	0·51	…	4·9	…	…			
15 „	0·44	0·43	0·46	0·14	…	…	…	…	…	…	…	3·9	…			
17 „	…	0·51	…	…	…	…	…	0·67	0·60	4·5	…	…	…			
19 „	0·61	0·58	0·71	0·15	0·086	0·7	0·6	0·74	…	…	…	3·1	…			
21 „	…	…	…	0·12	…	…	…	0·85	…	…	…	…	…			
23 „	…	…	…	0·13	…	…	…	…	…	4·4	…	…	…			
25 „	0·79	0·70	0·96	0·13	…	0·84	…	0·85	…	3·6	…	3·8	…			
28 „	0·89	0·83	…	0·12	…	0·75	…	0·92	1·08	…	…	2·7	…			
31 „	…	…	…	…	…	…	…	1·02	…	…	…	…	…			
34 „	…	…	1·16	…	…	…	…	0·96	1·20	…	…	…	…			
37 „	…	…	1·40	0·14	…	…	…	…	…	…	…	…	…			
40 „	1·36	…	…	…	…	…	…	0·91	1·1	…	…	…	…			
43 „	1·33	…	1·44	…	…	…	…	…	…	…	…	…	…			
46 „	…	…	1·25	…	…	…	…	…	…	…	…	…	…			

in the case of most of the concentrations given in Table I, a determination was also made by titrating the acid with alkali.

In Table II the gas evolved has been calculated to cc. of gas evolved per sq. decimetre per hour, on the assumption that the whole of the surface of the steel used (143 sq. cm.) was freely exposed to the action of the acid. This is only approximately true, as the small pieces of steel touched each other in places.

SERIES "B."

Samples of steel of the same kind as in series "A" but only 5 grams in weight (the surface being 35 sq. centimetres) were exposed to the action of concentrated sulphuric acid in large test tubes, and the tubes were then placed in a thermostat at 30° C. and shaken from side to side by a mechanical shaker worked by a motor. In this case the gas evolved was not measured, but the weight of the iron was taken before action, and after 28 days of action; the iron on being taken out of the sulphuric acid was washed with alcohol, then with water, then with alcohol and dried before the final weighing. The results obtained are as follows:—

Table III.

Concentrated acid.	Weight of iron lost in 28 days.
97·4	0·0993
94·0	0·8605
90·0	1·2223
89·3	0·1401
89·3	0·1331
87·9	0·5230
85·0	0·5264
80·0	2·9145

The experiments with 89·3% concentrated acid show distinctly less action than those with 94·0% acid, thus confirming the results obtained in the unstirred experiments.

Comparing the 94% acid when shaken with the results obtained in Table II, we notice that ·8605 gram of iron is lost in 28 days from 35 square centimetres of surface. This means that 340 cc. of hydrogen were produced by the solution of this ·8605 gram of iron, or 1·4 cc. per hour per sq. decimetre. This is the average rate for the 28 days, and is just about equal to the rate (1·36) obtained from the undisturbed acid after 43 days. As the average rate for 94% acid for 28 days in Series "A" (Table II) is only 0·35 cc. per sq. decimetre per hour, the accelerating effect of shaking is thus very noticeable. It is noticeable also in the other concentrations of sulphuric acid used.

Conclusions.—(1) The solvent effect of sulphuric acid, of concentration $(80\% - 91\%)$ H_2SO_4, on steel is noticeably increased by shaking the vessel containing the acid and steel.

(2) 97·4% H_2SO_4 and 89·3 H_2SO_4 have less action on the steel used than 94%, 90·9%, 87·9% or 85% acid.

(3) As the action of the acid on iron or steel produces a form of ferrous sulphate monohydrate $(FeSO_4, H_2O)$ on the surface of the iron, this causes a slowing down of the action and prevents action almost entirely in some cases.

(4) No real similarity exists between iron which is slowly dissolving in concentrated sulphuric acid and "*passive*" iron as produced by dipping iron into 1·4 sp. gravity nitric acid.

THE MISCIBILITY OF LIQUIDS.

THE MISCIBILITY OF LIQUIDS.

By CHARLES E. FAWSITT, and CHRISTIAN H. FISCHER.

[Read before the Royal Society of N. S. Wales, November 5, 1919.]

WHEN two liquids are shaken together they may (1) mix perfectly in all proportions with one another, or (2) dissolve partially in one another giving two layers, or (3) not mix at all (appreciably).   As examples of these cases we might take

> (1) ethyl alcohol and water
> (2) ether and water
> (3) mercury and water.

It was noticed by Rothmund[1] that the chemical composition had some connection with the mutual miscibilities and he drew up the following list of liquids in order:— Water, lower fatty acids, lower alcohols, lower ketones, lower aldehydes, nitriles, phenols aromatic aldehydes, ether, halogen derivatives of hydrocarbons, carbon disulphide, hydrocarbons.

In such a case, liquids which are close together on the list are miscible, while those furthest apart are the least miscible.

Later, Holmes[2] considered that the molecular volume of the liquid was the determining factor in connection with miscibility.   According to Holmes, complete miscibility is possible only when the molecular volumes are rather close numerically.

Holmes' conclusions are based on the supposition that the molecules are spherical.   While this premise is very

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[1] Zeit. für physikal. Chemie, 26, 489, (1898).

[2] Trans. Chem. Soc., (1913) 103, 2147.

doubtful, the conclusions are strikingly in accord with the experimental results, and it is astonishing that this valuable work has not hitherto been made more use of by chemists. Holmes arranges liquids in the order of the radii of their respective molecular volumes and this molecular volume list really assumes the importance of a miscibility table.

Holmes' Table.

	Molecular Radius compared with water.		Molecular Radius compared with water.
Water ...	... 1	Aniline ...	... 1·72
Glycerol ...	... 1	n-Butyl alcohol	... 1·72
Formic acid	... 1·28	n-Butyric acid ,	... 1·72
Methyl alcohol	... 1·31	isobutyl alcohol	... 1·72
Diethyl tartrate	... 1·33	isobutyric acid	... 1·72
Acetic acid	... 1·47	Ethyl acetate	... 1·76
Ethyl alcohol	... 1·48	Ethyl ether	... 1·80
Propionic acid	... 1·60	n-Amyl alcohol	... 1·82
Acetone ...	... 1·60	Methyl iodide	... 1·91
n-Propyl alcohol	... 1·60	Chloroform	... 2·07
Pyridine ...	... 1·64	Ethyl iodide	... 2·08
Nicotine ...	... 1·65	Benzene ...	... 2·14
Phenol ...	... 1·70	Carbon disulphide...	2·37
		n-Hexane ...	... 2·43
		n-Heptane ...	... 2·53

Dealing first with single (liquids) substances only, the following question arises:—"Would it be possible to take all (single) liquids, and arrange them in order in a table, such that the relative miscibility of any one of them (say *A*) with respect to any other (*B*) could be predicted?" This question can only be fully answered by experiment with all liquids. We have tested a somewhat larger number of liquids than Holmes, and for the liquids examined there seems little doubt that each has a fairly definite place on a list of liquids, such that its behaviour with respect to others can be predicted. When *A* dissolves to any extent in *B*, and *B* in *A*, to form two layers, even a small amount

of B dissolved in A will affect the properties of the A layer and in particular the molecular volume of A, so that the position of a liquid in regard to miscibility depends not only on its molecular volume and other properties, but on the way these are altered by introduction of the other liquid with which the miscibility is being examined. At the same time the influence of the solution of small amounts of other substances does not usually seem to be so very disturbing.

The following list contains a considerable number of liquids arranged in order.

It may be taken as a rule that if any one of these, say methyl alcohol No. 7, mixes perfectly with any other, say castor oil, No. 46, then all the liquids between Nos. 7 and 47 will mix perfectly. No. 9 mixes with all liquids up to No. 51, therefore all liquids between these will mix perfectly. It is interesting to note that while Nos. 13 and 15, dichlorhydrine and methyl acetate, are only partially miscible with water (No. 1), and partially miscible with No. 55 (liquid petrolatum) pyridine is miscible with No. 1 and No. 55.

The experiments were carried out at a room temperature of $18° - 22°$ C. and most of liquids used were Kahlbaum's (pre-war stock).

1 Water	11 Propyl alcohol
2 Glycerol	12 Propionic acid
3 Glycol	13 Dichlorhydrine ($C_3H_6O\ Cl_2$)
4 Formamide	14 Pyridine .
5 Formic acid	15 Methyl acetate
6 Diethyl tartrate	16 Methylal
7 Methyl alcohol	17 Methyl ethyl ketone
8 Acetic acid	18 Diethyl acetal $[C_2H_4(OEt)_2]$
9 Ethyl alcohol	19 Isobutyl alcohol
10 Acetone	20 Bromal

21	Ethyl acetate	39	Ethyl iodide
22	Ethylaceto acetate	40	Toluene
23	Ethyl ether	41	Bromoform
24	Phenylhydrazine	42	Isobutyl nitrate
25	Amyl alcohol	43	Nitrobenzene
26	Aniline	44	Isoamyl nitrate
27	Malonic ether	45	o-Methyl propyl benzene
28	Heptylic acid	46	Castor oil
29	Amyl acetate	47	Caprylidene (C_8H_{16})
30	Octyl alcohol	48	Pinene
31	Cineole	49	Carbon disulphide
32	Caprylic acid	50	Heptane
33	Nonylic acid	51	Kerosene (sp. gr. ·8)
34	α-Phellandrene	52	Teal oil
35	Chloroform	53	Sperm oil
36	Benzene (C_6H_6)	54	Olive oil
37	Methyl iodide	55	Liquid petrolatum (Parke
38	Carbon tetrachloride		Davis, sp. gr. ·836)

The following facts will be noticed:—

(1) Replacement of hydrogen in liquid hydrocarbons by —OH, COOH, $C_2H_3O_2$, NH₂, brings the position of the liquid nearer to the beginning of the miscibility table.

(2) Replacement of H in a hydrocarbon by CH₃ brings the liquid nearer the end of the table.

(3) Unsaturated hydrocarbons are nearer the beginning of the list than the corresponding saturated hydrocarbons.

(Chemical Department, University of Sydney.)

A NEW METHOD OF MEASURING
MOLECULAR WEIGHTS.

A NEW METHOD OF MEASURING MOLECULAR WEIGHTS.

J. G. STEPHENS, B.Sc.
John Coutts' Research Scholar.

(Communicated by Prof. O. E. Fawsitt.)

[*Read before the Royal Society of N. S. Wales, November 5, 1919.*]

THE ordinary boiling-point method for the determination of molecular weights depends upon the fact that the vapour pressure of a solution is lower than that of the pure solvent. This same fact may also be employed as the basis of the following method in which the molecular weight of a material is measured by comparison with that of a standard substance. The theory of this method will be understood on reference to Fig. 1, where each of the side tubes of the vessel represented contains a quantity of some liquid. Suppose that a quantity of a (liquid) solvent containing some known solute is introduced into one side of the apparatus whilst a quantity of the liquid containing some other soluble material is added to the other side. There will thus result two solutions which, having in general different concentrations of dissolved units, will accordingly possess different vapour pressures. A steady distillation will therefore occur from the solution of high to the solution of low vapour pressure, and equilibrium will only be reached when the transfer of liquid from one vessel to the other has rendered the vapour pressure of both solutions equal.

Now there is a principle stated by Ostwald that if two systems are in equilibrium one way, they must be in equilibrium in every way. It follows, therefore, that since these two solutions are in equilibrium as regards their

vapour pressure they must also be in equilibrium as regards their osmotic pressures. In other words the concentration of dissolved particles is the same in each solution.

Upon this condition we have

$$\frac{n_1}{v_1} = \frac{n_2}{v_2}$$

where v_1 and v_2 denote the volumes of liquid in the vessels A and B and n_1 and n_2 the number of dissolved molecules in these respective solutions. Hence, if m_1 and m_2 are the molecular weights of the two solutes, and w_1 and w_2 the weights of solute added to each side,

$$m_1 = \frac{w_1\, m_2\, v_2}{v_1\, w_2} = \frac{w_1\, m_2\, W_2}{W_1\, w_2}$$

where W_1 and W_2 are the weights of liquid in the vessels A and B. The actual form of the apparatus employed to determine molecular weights on the above principle is represented in the accompanying diagram (Fig. 1). The tubes A and B are ground into the connecting limb C, by which the two solutions are placed in communication. The space above the liquids was exhausted of air in order to secure more rapid distillation from one side to the other. Stirring of the solutions was accomplished by placing glass rods in each of the tubes A and B and then rocking the whole apparatus on a mechanical rocker of special construction.

In order to conduct a molecular weight determination with the above apparatus, all that was necessary was to place a weighed quantity of the substance (solute) in one of the tubes, and a weighed quantity of some other substance of known molecular weight in the other tube. Each of the tubes was then filled about two-thirds full of some liquid solvent, in which both of the substances were soluble. The exact amount of solvent added to either tube is immaterial. After fitting the tubes into the connecting limb,
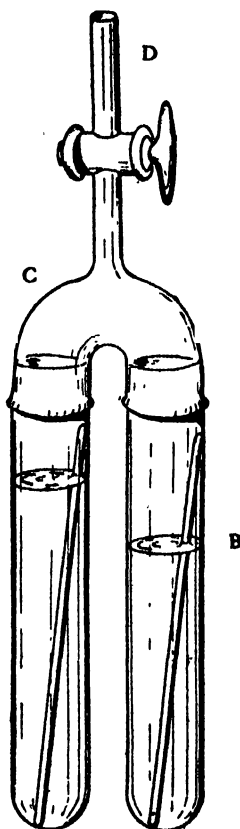
Fig. 1.

the space within the apparatus was evacuated by connecting D to a filter pump. When working the volatile solvents, such as ether, it was found advisable to place some shredded platinum foil in the tubes B and C, to prevent the bumping which would otherwise occur.

As regards the choice of a solvent, volatility is essential for rapid determinations, but the exact state of purity of the solvent does not seem to be of great importance. Both the solutes should be much less volatile than the solvent employed, and must not undergo association in solution.

The whole apparatus was allowed to stand for about forty-eight hours, after which time the tubes A and B were weighed, and the ratio of the weights of liquid in the tubes determined. This procedure was continued until the ratio of liquid in the tubes became constant, when the molecular weight was calculated from the formula developed above.

As an example of the method, the following case is given where benzene was used as the solvent and azobenzene was the substance of known molecular weight:—

Solutes { Weight of unknown substance 1·3586
{ Weight of azobenzene 1·0343
Weight of benzene in A after 48 hours 8·0512
Weight of benzene in B after 48 hours 16·3907
Molecular weight calculated, (after 48 hours) = 117·0

Weight of benzene in A after 90 hours 8·4401
Weight of benzene in B after 90 hours 15·9302
Molecular weight calculated, (after 90 hours) = 126·2

Weight of benzene in A after 108 hours 8·0202
Weight of benzene in B after 108 hours 15·1160
Molecular weight calculated, (after 108 hours) = 126·2

The theoretical molecular weight of the unknown was 128, which suffices to indicate the degree of accuracy which may be obtained by the method.

Using ether as a solvent, however, the same measure of success was not obtained, doubtless owing to the evaporation which occurred in removing the tubes for weighing. The apparatus used with ether was slightly different in form from that described above.   It consisted of two small retorts cut off at the neck and connected by a tightly fitting rubber tube.   The evacuation was effected by immersing the bulbs in hot water and inserting the stoppers while the ether was still boiling.   The rapidity with which the equilibrium condition was approached with this modification of the apparatus suggests that the time necessary for a determination could be considerably diminished by working at temperatures higher than that of the atmosphere.

The results obtained by the method first described may be summarised as follows:—

Solvent.	Substance determined.	Substance for comparison.	Mol. Wt. determined.	Mol. Wt. theoretical,
Benzene	Naphthalene	Azobenzene	126·2	128
Benzene	Azobenzene	Benzopenone	184·0	182
Ether	Azobenzene	Diphenylamine	173·7	182
Water	Glucose	Cane-sugar	160·0	180

It will be seen from these figures that the scheme outlined above affords a satisfactory practical method of molecular weight determination.   The ease with which

measurements may be conducted need not be emphasised. After the work which forms the subject of this paper had been completed, my attention was drawn by Mr. J. W. Hogarth of the University, to papers by Blackman and Barger,[1] in which a somewhat similar method is described. As the principle of Blackman's method is slightly different, however, the present description may not be entirely without value.

In conclusion I wish to express my thanks to Professor O. E. Fawsitt, for much advice and encouragement in the course of the present investigation.

Chemical Laboratory, University of Sydney.

[1] Trans. Chem. Soc., 1905, 87, 1474.

THE ANALYSIS OF TOLUENE AND BENZENE IN COAL TAR OILS.

By George Harker, D.Sc.

Assistant Lecturer and Demonstrator in Organic Chemistry (Pure and Applied) in the University of Sydney.

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At the outset of certain munition work dealing with toluene, which had been undertaken on behalf of the Federal Munitions Committee, it became necessary to find a reliable method for the estimation of toluene and incidentally of benzene in coal tar oil. Reference was made to standard works of analysis, and several papers on the subject which had appeared in recent chemical literature were consulted. It was found that while the methods employed were similar in general principle they differed very considerably in detail. In most cases after a preliminary distillation of the coal tar oil to a temperature of 150° to 170°, followed generally by a purification of the oil so obtained with sulphuric acid and soda, resort is had to a distillation test which varies greatly as given by different authors. In this distillation test, which must be carried out under rigid conditions, the volume of distillate at certain fixed temperatures is noted, and by reference to a table the percentage of toluene is estimated. The range of any of these tables correlating volumes of fractions collected up to and between certain temperatures with benzene and toluene content is more or less limited, *e.g.*, the table may only hold good for samples containing between 50 and 75 per cent. of toluene, in which case other samples must be mixed with benzene, toluene, or xylene before distillation.[1] James on the other hand,[2] employs three preliminary distillations to separate the oil into three fractions, No. 1

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[1] H. G. Coldman, *Journ. Soc. Chem. Ind.*, vol. 34, p. 168. [2] *Ib.*, vol. 35, pp. 236 - 240.

below 110˙6°, No. 2 from 110˙6 to 140°, No. 3 above 140°. A distillation test is then applied to Nos. 1 and 2, and a table for each is provided whereby the percentage of toluene is estimated.

From the divergence of the methods described, and in view of the more or less limited range covered by any of the distillation tables correlating volumes of fractions collected up to and between certain temperatures with benzene and toluene content, it was not considered advisable to proceed with the analysis of any samples of coal tar oil before making a series of blank experiments in which pure benzene and toluene in known quantity could be used. This was done in the first instance, to determine the reliability of the distillation test under observed conditions. As it was found that consistent results could be obtained from two or more distillations of any given mixture of benzene, toluene and xylene, provided the conditions were kept constant, the blank test method, as will be explained later, was used for the final determination of the benzene and toluene content of the coal tar oil samples, it being considered that this method was as quick and reliable as any that could be used. Fortunately for the purpose of the blank tests Kahlbaum's pure chemicals were available. The benzene and toluene boiled constantly at 80˙2° C. and 110˙5° C. respectively, and a sample of Kahlbaum's xylene (containing evidently the isomers of xylene) which was also used, distilled over between 134° and 139°, but mostly between 136° and 138°.

A Young and Thomas still-head of five sections was employed to assist fractionation, as giving greater definition than an ordinary distillation flask, and the rate of distillation was kept at one drop per second. The same still-head and rate of distillation were maintained throughout the analytical work on all samples and blank tests.

When mixtures of benzene and toluene were distilled, in which benzene was in the proportion of 3 : 1 or 4 : 1 to the toluene, it was found that under the conditions of experiment outlined above, the number of c.c. equal to the volume of benzene present distilled over when the temperature reached 90° C. or thereabout. When the benzene and toluene were in equal proportions, as for example, when distilling a mixture of 50 c.c. benzene and 50 c.c. toluene, the first 50 c.c. came over slightly above 95° C. Additions of xylene meant that the temperature of the mixture had to be raised still higher before the volume of distillate corresponding to the benzene fraction came over. These results were to be expected, and experiments were then made on mixtures of benzene, toluene and xylene in order to obtain some idea of the limits of temperature for the toluene fraction as well as for the benzene fraction with varying mixtures. The tests were useful in giving data for the approximate estimation of the benzene and toluene content of the samples examined later. Thus a mixture containing benzene and toluene in nearly equal proportions (the benzene preponderating), with a small proportion of xylene, had to be distilled to about 95° C. to give the volume of distillate equivalent to the amount of benzene contained in it, while the toluene figure was given by the volume of distillate collected between 95° and about 130° C. This kind of mixture was met with frequently in analysing the coal tar oil samples. The actual content of benzene and toluene present in the samples was obtained by carrying out a blank test after each distillation of the sample oil. In this blank test to the residue left in the flask, quantities of benzene (Kahlbaum's) toluene and xylene were added in accordance with the approximate estimation. The mixture was again distilled, whereby any error in the first estimation was corrected.

An actual analysis of tar oil for benzene and toluene will now be described.

A preliminary distillation of the oil up to 170° C. was first made in an ordinary distillation flask (without still-head) in order, while retaining all benzene and toluene, to separate a great portion of the higher boiling substances. The oil thus obtained was washed with sulphuric acid and caustic soda according to the method of Davis, as given in Lunge and Keane, vol. 2, part ii, p. 767. The washed oil, after standing overnight in order to complete the separation of water, was then distilled under the conditions outlined at the beginning, using the same round-bottomed flask and still-head as for the preliminary tests.

The paraffins present in the sample of coal tar oil were estimated either in the benzene or toluene fractions separately, or in the combined fraction. Generally speaking, the proportion of paraffins in the benzene or toluene fractions was about the same. The estimation was carried out with anhydrous sulphuric acid.[1]

Blank tests were first carried out with pure benzene and toluene, using 10 c.c. of anhydrous sulphuric acid and 5 c.c. hydrocarbon. In both cases the hydrocarbon was rapidly sulphonated and dissolved. The method was then tested on a sample of light ligroin distilled up to 100° C., and on mixtures of this with benzene and toluene, and found to be quite reliable. In carrying out an actual determination after sulphonation in a 100 c.c. cylinder, the liquid was poured into a small measuring cylinder whereby the volume of oil floating on top of the sulphonated liquid could be more accurately estimated.

Estimation of benzene and toluene in samples of coal tar oil, marked I, II and III, from the Sydney Municipal Council (Wattle Street Depôt).

Sp. gr. at 17° C. 0·928, 0·98, 1·012.

Lunge and Keane, vol. 2, pp. 799, and Allen, 4th Ed. vol. 8, p. 241.

Preliminary distillation of 250 c.c. in an ordinary distillation flask at 170° C.

Distillation Temp.	I. C.C.	II. C.C.	III. C.C.
100°	18	10	5 (including 2·5 c.c water)
130°	100	17	
150°	135	40	6 (including 3·0 c.c. water)
170°	163	70	10
Left after washing with conc. H₂SO₄ and NaOH	136	53	benzene and toluene present in very small amounts. Not further exam

The next step consists in the distillation of the washed oil from samples I and II in a round bottomed flask provided with still-head, the distillation being carried out as nearly as possible at the rate of one drop per second. After completing the distillation and measuring the residue, the latter is put back into the distillation flask and the estimated quantities of pure benzene, toluene, and xylene added. The blank test is then performed.

No. I. Sample.

68 c.c. of washed oil.	Blank consisting of 20 c.c. benzene, 22 c.c. toluene, 3 c.c. xylene, and 23 c.c. residue.	Remarks.
73° first drop	80°	
80 1 c.c.		The blank would
85 3·5 c.c.	4 c.c.	
90 12	14	have been nearer
95 18	18	
100 19	20	the sample if 20 c.c.
105 21	22	
110 23	26	toluene and 5 c.c.
117 31	36	
130 39	41	xylene had been
140 44	44	
Residue 24		used.
68 c.c.		

In distilling the sample oil, the residue is always measured in order to provide a check against possible losses in distillation. It sometimes occurs that the distillation loss exceeds 2 or 3 c.c., in this case the distillation must be repeated.

A comparison of the distillation figures for the sample and blank leads to the conclusion that 19 c.c. of benzene and 20 c.c. of toluene were present in the 68 c.c. washed oil, or 15·2 per cent. of benzene and 16·0 per cent. of toluene in the original No. I oil. The paraffins etc., contained in the benzene and toluene were estimated by sulphonating 5 c.c. of the mixed benzene and toluene distillate; 0·2 c.c. of oil was left equivalent to 4 per cent. of paraffins. This proportion of impurities of uncertain boiling point is too small to effect to any extent the comparison of the distillation figures of the sample and blank.

No. II. Sample.

53 c.c. of washed oil.	Blank consisting of 3 c.c. benzene, 12 c.c. toluene, 8 c.c. xylene, and 30 c.c. residue.	Remarks.
71° first drop	87° first drop	
80 0·5 c.c.		Proportions for
85 1·0		blank test badly
90 2·0		estimated owing to
95 3·0	2·0 c.c.	large ratio of higher
100		boiling constituents
105 5·0	3·0	to the lower boil-
110 6·0	3·5	ing.
117 11·0	5·5	
130 18·0	11·0	
140 23·0	16·0	
Residue 30·0		

It is clear that the benzene in the sample must have been between 4 and 4·5 c.c., and since 15 c.c. (equal to volume of the 3 c.c. benzene and 12 c.c. toluene added) were distilled over from the blank between 130° and 140°, it is

estimated that 17 c.c. of toluene were present in the sample, *i.e.*, 21 c.c. of benzene and toluene together. This gives 1·6 per cent. benzene and 6·8 per cent. toluene in oil No. II. It is quite exceptional for the first approximation to differ so much from the true content as shewn by the blank test, and in order to confirm the figures a second blank test should have been performed. The paraffins were present to the extent of 4 per cent.

Macrozamia Spiralis as a Source of Industrial Alcohol.

By GEORGE HARKER, B.Sc. (Syd.), D.Sc. (London).*

I.—GENERAL.

Macrozamia or the Zamia palm (known in New South Wales also as burrawang or native pine-apple) is a gymnosperm belonging to the Cycad family. There are two main species common in Australia. These are *Macrozamia spiralis,* of New South Wales and Queensland, and *M. fraseri,* of South-west Australia. In New South Wales, the palm grows usually to a height of 2 or 3 feet, with a stem 1 or 2 feet in diameter. The Western Australian species is decidedly stouter than the eastern, and in exceptional cases attains a height of 10 or 12 feet. The plant chiefly occurs in poor land of little value for agricultural purposes, but is equally at home in damp low-lying soils and on stony hillsides. In such localities in the coastal regions of both New South Wales and Western Australia the plant often forms a dominant element of the vegetation. Many thousands of acres are covered by it, for example, in the vicinity of Nelligen, near Bateman's Bay, and in the Kincumba district, near Gosford. In Western Australia it is very plentiful along the south-western railway line, almost all the way from Perth to Busselton, a distance of about 130 miles, whilst it also occurs in great abundance on the western slopes of the Darling Range.

In connexion with the work of the Special Committee appointed by the Institute of Science and Industry to investigate the question of the manufacture and use of power-alcohol, it was considered desirable to inquire into the possibility of utilizing macrozamia as a raw material for the manufacture of alcohol. The investigation to which this report relates was accordingly undertaken primarily for the purpose of determining the amount of alcohol yielded by *Macrozamia spiralis* collected in different districts of New South Wales at different stages of growth, and at varying periods of the year. It was also desired to obtain information regarding the amount of starch present in the plant. It was decided to examine the outer, as well as the inner, core of the bulbs. as, up to the present, only the inner core has ever been treated. This entailed twice as much work, but the results obtained more than justified the expenditure of the extra labour. By arrangement with the Forestry Commissioners of New South Wales, samples of macrozamia were collected from different localities in the State, and at different times of the year. These were sent to the Sydney University, where the investigations were carried out on behalf of the Institute of Science and

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Industry. The bulbs always arrived in excellent condition, and grateful acknowledgment is made to the Forestry Commissioners for their valuable assistance in providing the raw material.*

On arrival of a batch of bulbs at the University, the leaves were stripped, each bulb being weighed, the outer core removed and weighed, and the weight of inner core obtained by difference. The outer and inner portions were separately ground, first through a coarse sieve and afterwards through a fine sieve. The material was then sampled, and several pounds weight were thoroughly air-dried and kept for the chemical investigation. The loss of moisture on air-drying was determined on a kilogram portion. The material when air-dried could be kept, without fear of decomposition, until an opportunity for the chemical investigation presented itself. The grinding of a wet fibrous material such as macrozamia is a difficult matter, but it was carried out with satisfaction in the 5 horse-power Van Gelder grinder machine which had been installed for the purpose.

Four different parcels of bulbs were received from the Forestry Commissioners—two from Bateman's Bay (South Coast) and one from Wyong, a district about 50 miles north of Sydney, and one from Murwillumbah, Tweed River. The six bulbs from Wyong were small, and had evidently been dug out of sandy soil; on account of their small size these bulbs received were taken for investigation in three lots of two bulbs each. The bulbs from Murwillumbah were more cylindrical in shape, and grew chiefly above ground. The bulbs from Bateman's Bay were similar to those from Wyong in shape, but were larger and grew chiefly above ground. They were, however, considerably older than those from Wyong. All the specimens were identified by Mr. J. H. Maiden, F.R.S., Director of the Botanic Gardens, Sydney, as *Macrozamia spiralis.* The approximate age of the bulbs was computed by counting the annual growths.

The largest of the bulbs weighed 388 lbs., and its age was computed to be 120 years; the smallest weighed only 18 lbs., its age being 65 years. The average yearly increase in weight during the total period of growth, for the inner core, ranged from 0.1 to 1.6 lbs., and for the outer core, from 0.1 to 4.3 lbs.

II.—METHODS OF INVESTIGATION.

In order to obtain alcohol from macrozamia, the contained starch must first be converted to sugar and then fermented. In a preliminary investigation, inversion of the starch was effected by both diastase and by acid hydrolysis, and the yields of alcohol compared. The results were very similar, those from the acid hydrolysis being generally slightly greater. For the main investigation, acid hydrolysis was chosen, chiefly because better control is obtained. The chemical analysis was carried out by Miss Hindmarsh, B.Sc., Demonstrator in Physiology, Sydney University, and Mr. A. Kellick, Demonstrator in Chemistry, Sydney University.

* The Forestry Commission, N.S.W., advises that the cost of obtaining and delivering on wharf at Bateman's Bay of the cores only (outer covering removed) would be about 20s. per ton.—ED. S. and T.

The percentage of alcohol in solution, the quantities of alcohol obtained from the whole bulb, and from the inner and outer parts of the core, respectively, are shown in the following table:—

TABLE I.—MACROZAMIA INVESTIGATIONS.

Yields of Alcohol from Bulbs.

District.	Reference Number.	Per Cent. Alcohol in Solution.		Gallons Alcohol from each Portion of Bulb		Gallons Alcohol from Whole Bulb.
		Inner.	Outer.	Inner.	Outer.	
Bateman's Bay	1	0·80	1·34	0·131	0·772	0·903
	2	1·55	1·79	0·132	0·549	0·681
	3	1·30	1·01	0·222	0·439	0·715
	4	1·39	1·17	0·471	0·775	1·246
	5	2·00	1·06	0·457	0·720	1·177
	6	2·09	0·56	1·010	0·273	1·283
	7	2·16	0·79	1·781	0·631	2·412
Wyong	1	0·34	0·94	0·009	0·134	0·143
	2	1·16	1·34	0·156	0·605	0·761
	3	1·05	0·73	0·041	0·131	0·172
Murwillumbah	1	0·13	0·10	0·003	0·003	0·006
	2	0·47	0·20	0·022	0·005	0·027
	3	0·92	0·04	0·098	0·002	0·100

The gallons of alcohol yielded per ton (2,240 lbs.) by the inner and outer portion of each undried bulb, and also the gallons per ton yielded by each complete undried bulb, were thus obtained, and are given in Table II.

TABLE II.—MACROZAMIA INVESTIGATIONS.

Yields of Alcohol expressed in Gallons per Ton.

District.	Reference Number.	Gallons Pure Alcohol per Ton Inner Core.	Gallons Pure Alcohol per Ton Outer Core.	Gallons Pure Alcohol per Ton Whole Bulb.
Bateman's Bay	1	8·38	14·50	13·13
	2	18·46	21·77	21·04
	3	12·44	9·87	10·54
	4	14·08	11·65	12·46
	5	19·70	10·68	12·99
	6	19·32	4·86	11·83
	7	20·35	7·64	13·92
Wyong	1	2·50	7·68	6·80
,,	2	10·62	14·42	13·43
,,	3	7·10	5·63	5·93
Murwillumbah	1	1·41	0·69	0·70
	2	4·12	1·42	3·05
	3	7·56	0·29	4·97

The residual moisture in the air-dried samples (obtained by heating weighed quantities in a steam oven) was found to vary very little, and the average figure for six different samples was found to be 11.3 per cent.

III.—CONCLUSIONS.

The first deduction from the figures for the yield of alcohol is that, as a source of industrial alcohol, the bulbs from the Murwillumbah district were useless, while those from Wyong gave considerably less alcohol than those from Bateman's Bay. The interest in this result lies in the fact that the principal supplies of macrozamia in New South Wales are found in the South Coast districts.

The next point of importance brought out by the investigation is that, contrary to expectation, the outer cores of the bulb yield considerable quantities of alcohol, and in several instances, as shown in Table II., larger yields of alcohol per ton were obtained from the outer core than from the inner core of the same bulb.

The Bateman's Bay bulbs were the only ones of which samples were obtained at different periods of the year, and closer study of the results from these bulbs indicates fairly definitely that a transference of starchy material from the outer to the inner core takes place at certain seasons, and that consequently at these periods the inner core is richer and the outer core poorer in starch than at other seasons. If the figures for the first five bulbs collected in October, 1918, are taken, it is found that 218 lbs. of inner core give 1.414 gallons alcohol, while 587.5 lbs. of outer core gave 3.309 gallons, corresponding to yields per ton of 14.52 gallons from the inner core and 12.63 from the outer core. For the whole bulbs, 805.5 lbs. gave 4.723 gallons, or 13.13 gallons to the ton. The ratio of weight of outer core to inner at this period of the year was 2.7 : 1.

For the two bulbs collected in January, 1919, the figures were:— 313 lbs. inner core gave 2.791 gallons; 318 lbs. outer core, 0.9047 gallons; corresponding to yields of 19.97 gallons and 6.37 gallons per ton for the inner and outer cores, and 13.12 gallons for the whole bulb. The weights of outer and inner core were in the ratio of nearly 1 : 1. The leaf bases of the specimens collected in October were very rich in starch, and the analysis indicates that in the period between October and January a large portion of the starch from the outer core was transferred to the inner. The outer core decreased in weight relatively to the inner, while the percentage of starch in the weight of the whole bulb remained very constant. Further investigation on samples of bulbs collected throughout the year is necessary to confirm these results, and to determine at what period in the year the starch-content of the inner core reaches its maximum.

In regard to the starch-content of the plant, Table III. gives the percentages of starch obtained by calculation from the yield of alcohol on fermentation. It was hoped to determine the starch by other methods, but, although some preliminary tests have been carried out by Miss Hindmarsh on this portion of the work, no time has been available to provide separate figures. In fermenting starch solutions from raw products, a theoretical yield of alcohol is not to be expected, and consequently starch percentages calculated from alcohol results tend to be low. On the other hand, not all of the fermentable sugar present

after hydrolysis is necessarily due to starch, and this tends to make the starch percentages higher than they really are. In the present investigation it is considered, in view of certain tests made, that nearly all of the fermentable sugar was derived from the inversion of starch, and consequently the figures given for starch in Table III. may be low, but only to a slight degree.

TABLE III.—MACROZAMIA INVESTIGATIONS.

Percentage of Starch calculated from Yield of Alcohol.

District.				Reference Number.	Per Cent. Starch Inner Core.	Per Cent. Starch Outer Core.	Per Cent. Starch Whole Bulb.
ateman's Bay		..	..	1	5·23	9·05	8·19
,,	,,	..	..	2	11·52	13 58	13·12
,,	,,	..	..	3	7·76	6·16	6·58
,,	,,	..	..	4	8·78	7·27	7·74
,,	,,	..	..	5	12·30	6·66	8·11
,,	,,	..	..	6	12·05	3·03	7·38
,,	,,	..	..	7	12·70	4·77	8·68
/yong	..	..	..	1	1·56	4·79	4·24
,,	..	..	..	2	6·63	9·00	8·38
,,	..	..	..	3	4·43	3·51	3·70
urwillumbah		..	..	1	0·88	0·43	0·44
,,		..	..	2	2·57	0·89	1·90
,,		..	..	3	4·72	0·18	3·10

The results from Bateman's Bay gave the best and most consistent results, and on summing these up it is found that 531 lbs. inner core gave 4.025 gallons alcohol, equivalent to 17.73 gallons (18.67 of 95 per cent.) alcohol per ton; 905.5 lbs. outer core gave 4.214 gallons, equivalent to 10.43 (10.98 of 95 per cent.) gallons per ton; while 1.436.5 lbs. of the whole bulbs gave 8.435 gallons, equivalent to 13.13 (13.82 of 95 per cent.) gallons per ton. The percentages of starch corresponding to these figures are—inner core, 11.06; outer core, 6.51; whole bulb, 8.19 per cent.

Bulletin No. 6, on the subject of Power Alcohol, issued by the Institute of Science and Industry, contains a table, page 19, giving the percentages of alcohol obtainable from various substances. The yield from macrozamia is set down as 18 gallons per ton. This figure refers to the alcohol obtainable from the inner core, and is thus in agreement with the average figure from the inner cores of the Bateman's Bay series.

The age of the bulbs and the rapidity of growth has a very important bearing on the question of utilizing macrozamia as a source of industrial alcohol. Professor Lawson stated at the outset that the growth of these plants is very slow indeed. This was confirmed by an examination of the bulbs used for the purposes of the present investigations. The average yearly increase in weight of the Murwillumbah bulbs is much less than that of the bulbs from the two other districts. The growth of the plants being so slow, it is clear that the economic use of macrozamia depends upon the quantity of material already available.

From the point of view of alcohol production, the high fibre-content of the bulb is a disadvantage, since the solutions for fermentation must be considerably diluted with water in order to make it possible to work with them. This applies more particularly to the outer cores, the fibre-content of which is generally very high. The high fibre-content of the outer cores is shown in Table IV., which gives complete figures for some of the Bateman's Bay series.

TABLE IV.—MACROZAMIA INVESTIGATIONS.

Particu'ars of Bateman's Bay Bulbs.

Reference Number.				Total Water.	Fibre.	Starch.	Soluble Extract in addition to Starch.
1. Outer	..	..	..	53·1	16·3	9·1	21·5
4. Outer	..	..	..	57·2	17·8	7·3	17·7
6. { Inner	..	..	..	62·1	6·2	12·1	19·6
Outer	..	..	..	62·3	20·7	3·0	14·0
7. { Inner	..	..	..	61·3	7·8	12·7	18·2
Outer	..	..	..	59·1	20·9	4·8	15·2

It would probably be possible to hydrolyze the fibre and convert it into fermentable sugar. If this could be done cheaply, not only would the yield of alcohol be increased, but the trouble caused by the presence of so much fibre would be removed. In this connexion it should be noted that wood has been used commercially as a source of alcohol, and that hopes are entertained of hydrolyzing peat and making use of it. An experiment conducted with more concentrated acid on the fibre of macrozamia showed that it appears to hydrolyze readily, and a good yield of bodies, which reduced Fehling's solution, was obtained, but no attempt was made to determine whether alcohol could be produced from them. Until some use can be found for the fibre, or it can be proved advantageous to completely hydrolyze it, attention must be confined to the inner core as a source of alcohol. In this connexion there is the possibility that the residue left after fermentation may prove of value as a cattle fodder. High fibre-content is a hindrance to the extraction of starch, so that it appears unlikely that the outer core has any value at the present time. This makes it all the more necessary to determine at what period of the year starch-content of the inner core reaches its maximum.

In conclusion, acknowledgment is made to Mr. Gilbert Wright, Lecturer in Agricultural Chemistry, University, without whose interest and assistance the investigation could not have been carried out.

A NOVEL APPLICATION OF BROMINE WATER IN SYNTHETIC ORGANIC CHEMISTRY.

A NOVEL APPLICATION OF BROMINE WATER IN SYNTHETIC ORGANIC CHEMISTRY.

By JOHN READ, M.A., Ph.D., and MARGARET MARY WILLIAMS, B.Sc.

BROMINE water is often used as a test for unsaturation in the molecule of organic substances : decolourisation of the reagent being taken to indicate the presence of the ethylenic or the acetylenic linkage. In the former case, the reaction has usually been assumed to yield solely a dibromo-compound, in accordance with the subjoined general scheme:

$$RR_1C : CR_2R_3 + Br_2 = RR_1CBr \cdot CBrR_2R_3.$$
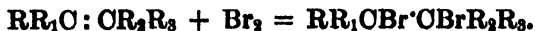
We have recently been able to show, however, that in the simplest and best-known case of this kind, namely, that of ethylene, the yield of the dibromide may under suitable conditions fall quite low, the bulk of the product being ethylene bromohydrin. In this instance the bromine water is thus an efficient source, not only of bromine, but also of hypobromous acid, and the two reactions represented below take place concurrently:—

(1) $H_2C : CH_2 + Br_2 = H_2CBr \cdot CBrH_2$;

(2) $H_2C : CH_2 + HO \cdot Br = H_2CBr \cdot CH_2OH.$
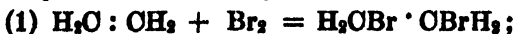
Of the total bromine used in a particular experiment, 37·5 per cent. was converted to ethylene dibromide, 54·4 per cent. was converted to ethylene bromohydrin, and the remaining 8·1 per cent. was eliminated as hydrobromic acid, formed by a partial decomposition of the hypobromous acid to hydrogen bromide and oxygen.[1]

From these figures it is clear that the relative percentage amounts of ethylene converted to dibromide and bromo-

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[1] Trans. Chem. Soc., vol. 111 (1917), p. 240.

hydrin were 40·8 and 59·2, respectively. This yield of ethylene bromohydrin is equal to the highest recorded as obtainable by the action of a carefully prepared solution of hypobromous acid upon ethylene.

In view of the laborious and unsatisfactory methods used in the preparation of aqueous solutions of hypochlorous and hypobromous acids and the consequent difficulty of obtaining halogenohydrins directly from unsaturated substances, it was considered of importance to ascertain whether the readily accessible reagent bromine water could be utilised as a source of hypobromous acid in other reactions of a similar type.

The second substance to be selected for investigation in this connection was cinnamic acid. The result in this case was even more striking than with ethylene. We have been able to demonstrate that under suitable conditions cinnamic acid reacts speedily and quantitatively with bromine water, giving a yield of over 80 per cent. of the bromohydrin, *i.e.*, β-phenyl-α-bromohydracrylic acid (commonly known as phenyl-α-bromolactic acid). The other product of the reaction is cinnamic acid dibromide:—

(1) $C_6H_5 \cdot CH : CH \cdot COOH + HO \cdot Br =$
$$C_6H_5 \cdot CHOH \cdot CHBr \cdot COOH;$$
(2) $C_6H_5 \cdot CH : CH \cdot COOH + Br_2 =$
$$C_6H_5 \cdot CHBr \cdot CHBr \cdot COOH.$$
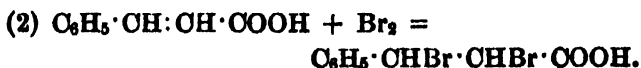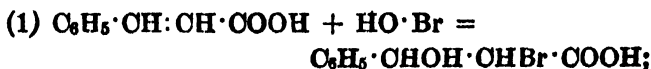
In order to obtain the maximum yield of the bromohydrin, the cinnamic acid is subjected to vigorous mechanical stirring in contact with about thirty times its weight of ice-cold water, into which a slow current of air charged with bromine vapour is introduced through a perforated glass bulb.

Under these conditions absorption of the bromine takes place rapidly at first, but slackens gradually towards the end of the reaction. A very slight excess over the calcu-

lated quantity of bromine is sufficient to produce a permanent yellow tinge in the liquid.

When the absorption is complete the undissolved cinnamic acid dibromide is separated by filtration from the aqueous liquid, which contains the phenyl-α-bromolactic acid in solution. This substance is readily isolated by extraction with ether, in which it is extremely soluble. The extracted aqueous liquid upon evaporation yields nothing beyond a further small quantity of cinnamic acid dibromide. No bromostyrolene appears to be formed in the reaction.

The purification of phenyl-α-bromolactic acid appears to have been effected in many cases by crystallisation from chloroform, notwithstanding its ready solubility in the cold solvent. The best results are obtained by crystallisation from hot water or from hot benzene or toluene; the acid may also be crystallised from hot ligroin, in which, however, it is only sparingly soluble. The pure acid dissolves to a clear solution in warm water. A slight admixture of cinnamic acid dibromide is sufficient to cause turbidity in such solutions, due to the formation of bromostyrolene; the latter substance may easily be removed by shaking the liquid with light petroleum. It may also be noted that phenyl-α-bromolactic acid separates readily from aqueous solution, in the form of a crystalline precipitate, upon the addition of dilute sulphuric acid.

After one recrystallisation from hot toluene, the acid prepared in the manner described above melted at $120° - 122°$. Upon adding an equivalent amount of silver nitrate solution to an aqueous solution of the acid, a rapid separation of the crystalline silver salt occurred; titration of the washed and air-dried salt with standard ammonium thiocyanate solution indicated a silver content of $30·28$ per cent., the formula $C_9H_8O_3BrAg$ corresponding to $30·68$ per cent.

The processes involved in the above reaction are summarised in the appended scheme:—

$$Br_2 + H \cdot OH \rightleftharpoons HBr + HO \cdot Br$$

$$C_6H_5 \cdot CHBr \cdot CHBr \cdot COOH \qquad C_6H_5 \cdot CHOH \cdot CHBr \cdot COOH.$$

From this it is apparent that the production of every molecule of bromohydrin involves the formation of a molecule of hydrogen bromide. An excess of hydrobromic acid in the aqueous solution, over the amount arrived at in this way, will be due to decomposition of hypobromous acid into hydrogen bromide and oxygen:—

$$HO \cdot Br = HBr + O.$$

Any wastage of bromine occurring in this way may therefore be traced by estimating the amount of hydrobromic acid in the aqueous solution.

In a carefully conducted operation, 20 grams of cinnamic acid yielded 6·55 grams of cinnamic acid dibromide and 27·1 grams of phenyl-α-bromolactic acid, $C_6H_5 \cdot CHOH \cdot CHBr \cdot COOH + H_2O$. It is thus evident that the relative percentage amounts of cinnamic acid converted to dibromide and bromohydrin were 17·1 and 82·9, respectively.

The amount of bromine used in this operation was 21·3 grams; from the data just quoted, the quantities utilised in forming dibromide and bromohydrin were 3·40 and 16·49 grams, respectively. Consequently, the wastage of bromine in the operation, due to the combined causes of decomposition of hypobromous acid and possible diffusion of unaltered halogen, was only 6·6 per cent. This result compares favourably with that obtained with ethylene, in which case the loss of bromine was 8·1 per cent. In both cases, however, since a certain loss of the reaction-products is unavoidable during the process of their isolation, the actual wastage of bromine will be somewhat less than the above figures indicate.

These results having been obtained by using a suspension of cinnamic acid in water, it was next of interest to investigate the action of the reagent upon a neutral solution of a soluble salt of the acid; for this purpose the cinnamic acid was dissolved in the minimum amount of sodium bicarbonate solution. Upon conducting the operation in the manner described above, the bromine was absorbed more rapidly than under the original conditions; and a heavy oil, accompanied by a small amount of crystalline material, separated from the solution. At the end of the reaction, a little dilute sulphuric acid was added to the liquid; the oil was extracted with light petroleum and identified as β-bromostyrolene; the accompanying insoluble solid product proved to consist essentially of cinnamic acid dibromide. A third product, namely, phenyl-α-bromolactic acid, was extracted from the aqueous solution in the usual way by means of ether.

In this way, 20 grams of cinnamic acid yielded 18·7 grams of phenyl-α-bromolactic acid, 1·9 grams of cinnamic acid dibromide, and 10·5 grams of β-bromostyrolene. Thus, the relative percentage amounts of cinnamic acid converted to bromohydrin, dibromide, and β-bromostyrolene were 52·8, 4·6, and 42·6, respectively. The amount of bromine used was 21·3 grams; and an examination of the above figures shows that both the cinnamic acid and the bromine are quantitatively accounted for.

The interesting result is thus revealed that by modifying the conditions of the reaction in this simple manner the yield of bromohydrin falls from 82·9 to 52·8 per cent., the yield of dibromide falls from 17·4 to 4·6 per cent., and a new product, β-bromostyrolene, is formed to the extent of 42·6 per cent. The last named substance being evidently derived by decomposition of the sodium salt of cinnamic

acid dibromide, the complete series of reactions involved may be summarised as follows:—

$$Br_2 + H \cdot OH \rightleftharpoons HBr + HO \cdot Br$$

$$C_6H_5 \cdot CHBr \cdot CHBr \cdot COONa \qquad C_6H_5 \cdot CHOH \cdot CHBr \cdot COOH + NaBr$$

$$C_6H_5 \cdot CH:CHBr + NaBr + CO_2.$$
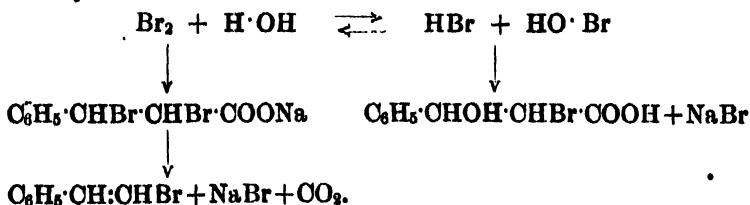
Quite apart from the general interest of these results, the reaction which forms the main subject of this communication is obviously of value as affording a greatly improved method for the preparation of phenyl-α-bromolactic acid. As far as can be ascertained, the only method hitherto available for this purpose has involved the prolonged boiling of cinnamic acid dibromide with water;[1] as is well known, this process is vitiated by the formation of appreciable quantities of bromostyrolene and other by-products.

Phenyl-α-bromolactic acid is of interest because of the ease with which it is converted into phenylacetaldehyde, a substance which, owing to its intense hyacinth odour, is used to some extent in perfumery. The conversion is brought about by treating the phenyl-α-bromolactic acid successively with caustic alkali and dilute sulphuric acid:[2]

$$C_6H_5 \cdot CHOH \cdot CHBr \cdot COONa + NaOH =$$
$$C_6H_5 \cdot CH \cdot CH \cdot COONa + NaBr + H_2O.$$
$$\backslash O /$$

$$C_6H_5 \cdot CH \cdot CH \cdot COOH = C_6H_5 \cdot CH_2 \cdot CHO + CO_2.$$
$$\backslash O /$$
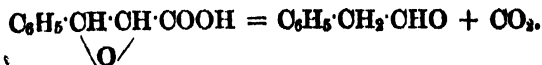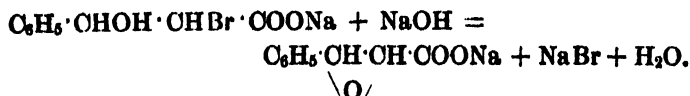
It is apparent that the reaction described above facilitates very considerably the preparation of phenylacetaldehyde from cinnamic acid.

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[1] Glaser, Liebig's Annalen, vol. 147, p. 84.

[2] Erlenmeyer and Lipp, Liebig's Annalen, vol. 219, p. 182,

In continuation of the work outlined in this paper, it is proposed to investigate various other aspects of this method of halogenohydrination.   Some possible applications of the reaction in synthetic and other organic chemical processes are worthy of consideration, particularly, it would seem, in connection with the preparation of synthetic drugs. The use of ethylene bromohydrin in the novocaine synthesis is a case in point; further, the grouping : C(OH)·C(NHR): , so readily derived from the closely related halogenohydrin grouping, : C(OH) C(X): , appears to possess a considerable degree of physiological importance.   In conclusion, it may be remarked that the presence of so many ethylenic constituents in the Australian natural essential oils lends an additional interest to the reaction.

SYDNEY SECTION.

MEETING HELD ON MAY 26TH, 1919.

MR. B. J. SMART IN THE CHAIR.

Note on a Papuan Natural Petroleum

BY

JOHN READ, M.A., Ph.D., & MARGARET MARY WILLIAMS, B.Sc.

The investigation of which a summary is here given was carried out in 1916. Publication was deferred for the time being, in the hope that larger supplies of the material would become available for examination, but this expectation has not yet been realised. Owing to the small amount of material, many of the operations could not be carried out in duplicate; and for the same reason a thorough fractionation of the oil was impracticable: these limitations should be borne in mind in considering the appended numerical data.

FIRST SAMPLE.

The first sample (Vailala Oilfield, Papua) possessed a light brownish-yellow colour with a bluish fluorescence, and readily yielded water-white material on distillation. The smell was in no way unpleasant, and resembled closely that of kerosene. The amount of suspended matter was minimal. Neither the crude oil nor the colourless distillates responded to the indophenin reaction or to tests for nitrogen or sulphur. The oil suffered no appreciable loss on shaking with dilute acid or alkali. In its general characteristics it is thus very similar to Borneo petroleum. The specific gravity of the crude oil was 0.796 at 18.75°C.

Fractional distillation.

The crude oil (1000 grms.) was distilled from a long-necked round-bottomed flask, through an ordinary condenser, up to 170° C. The resulting distillate, or "170° run" (370 grms.), was then fractionally distilled from a similar flask connected with a 4-pear still-head, the total height of the con-

densing column being 58 cm., the diameter of the bulbs 2.5 cm., and the rate of distillation 2 drops per second. Particulars of the fractionation are summarised below :—

Temperature	Weight of fraction. grms.	Weight percent-age of "170° run"	Weight percent-age of crude oil	Specific gravity
To 170° C.	370	100	37 0	0·744 at 19·5°
60°– 90°	60·9	16 5	6·1	0·707 at 19·5°
90°–120°	174·4	47·1	17·4	0·744 at 20°
120°–150°	75·8	20·5	7·6	0 760 at 21°
above 150°	41·5	11·2	4·2	0·788 at 19·5°
	352·6	95·3	35·3	

The remainder of the sample (1500 grms.) was distilled in a similar manner, up to 180°, and the resulting " 180° run " was fractionally distilled in the manner adopted in the first experiment.

The results demonstrated that it is immaterial, as far as the first two fractions are concerned, whether the " straight run " is cut at 170° or 180°; in the latter case, however, an appreciably higher yield of the third fraction (120°–150°) is obtained. The unusually high proportion of light oils is in agreement with the low specific gravity of the crude material.

Nitration of fractions.

The distillates only decolorised bromine water after several hours' contact: it was therefore con-

cluded that the oil contains saturated hydrocarbons, possibly in admixture with aromatic hydrocarbons, and this was confirmed by a preliminary nitration test. Accordingly, the several fractions were submitted to a systematic series of nitration experiments, the mixture of oil and nitrating acid being mechanically stirred during the process, and the temperature kept below 25°C, until no further heat was developed. The mixture was eventually heated gradually to 40° and then allowed to cool, with continuous stirring, in order to complete the nitration.

(a) When treated in this way, the first fraction (60°—90° C.) yielded two layers, the upper of which was separated, washed with dilute sodium carbonate solution and water, dried, and distilled from a bath of boiling water. The residual, pale yellow oily nitro-product was weighed, as was also the distillate of unaltered hydrocarbons. Owing to the volatility of the latter, the content of aromatic hydrocarbons could not be obtained by difference, and the values quoted below are calculated on the assumption that the nitro-product represents pure mononitrobenzene.

(b) The product obtained by nitrating the second fraction (90°—120°) settled into three layers. The bottom layer of spent acid was run off, and the other layers mixed and washed with dilute sodium carbonate solution, followed by water, after which the dried unchanged hydrocarbons were distilled from the nitro-product. The results of three experiments are tabulated on page 320 т. The weight-percentages of aromatic hydrocarbons were calculated (1) by difference, and (2) as toluene, assuming the nitro-product to consist of mononitrotoluenes.

The first determination was carried out with material from the "170° run," the second and third with material from the "180° run": the results indicate that no appreciable difference in composition exists between the second fractions yielded by these two runs.

The mean value, 11·7%, corresponds to 5·5% of the "170° run," 4·5% of the "180° run," and 2·0% of the crude oil. The high specific gravity of the residual hydrocarbons is again noticeable.

On further nitration, the oily nitro-product gave

Fraction 60°—90°.

Weight taken	Weight of nitro-product	Percentage of benzene (wt.)			Unaltered hydrocarbons		
		In fraction 60°-90°	In "170° run"	In crude oil	Weight	Percentage	Specific gravity
40 grs.	4·4 grs.	7·0	1 16	0·43	29·5 grs.	73·8	0·710 at 19·5°
109 ,,	7·84 ,,	4·6	0 76	0·28	90·8 ,,	83·3	0·709 at 19·5°

Fraction 90°—120°.

Weight taken	Weight of nitro-product	Percentage of toluene (wt.)		Unaltered hydrocarbons		
		By difference	From wt. of nitro-product	Weight	Percentage	Specific gravity
40 grs.	7·0 grs.	12·5	11·8	35·0 grs.	87·5	0·741 at 17·5°
120 ,,	17·9 ,,	13·3	10·0	104·0 ,,	86·7	0·747 at 17°
120 ,,	18·0 ,,	12·5	10·1	105·0 ,,	87·5	0·747 at 17°
		Mean = 11·7.				

The high value obtained in the first experiment may be due to the use of an appreciable excess of nitrating mixture and the consequent formation of higher nitro-compounds.

About one-half of the mixed yields from the two experiments distilled over between 200° and 210°, and on further nitration gave a hard, pale yellow, crystalline product with a dry setting-point of 68° C. The higher-boiling portion of the original nitro-product appeared to contain nitrotoluenes.

The high specific gravity of the residual hydrocarbons points to the presence of naphthenes in association with paraffin hydrocarbons. A similar peculiarity is presented by Borneo petroleum.

a pale-yellow, hard crystalline solid with wet and dry setting-points of 60° and 65° C. respectively.

(c) The third fraction (120°—150°) behaved very similarly to the second when nitrated. In this case, after separating the two upper layers from the spent acid, the nitro-product was extracted from the residual hydrocarbons by shaking out with concentrated sulphuric acid. 60 grms. of the fraction gave 51·9 grms. of washed and dried residual hydrocarbons, having after redistillation the sp. gr. 0·766 at 19·15°. The weight-percentage of aromatic hydrocarbons, obtained by difference, was 13·5% in the fraction, corresponding to 1% in the crude oil. Further nitration gave a light-yellow, crystalline

product, which remained solid in contact with boiling water.

(d) The fourth fraction (above 150°) when submitted to similar treatment gave 13·3% by weight of aromatic hydrocarbons, estimated by difference, or 0·6% in the crude oil. The residual hydrocarbons, after washing and redistillation, possessed a specific gravity of 0·768 at 19°. When nitrated further, the sulphuric acid extract of the nitro-product yielded a yellow, pasty mass, in, which solid crystalline particles were discernible.

SECOND SAMPLE.

The second sample (No. 5 bore, Government Oilfield, Upoia, Papua) had sp. gr. 0·7965 at 22°, and proved to be practically identical in all respects with the first sample.

Fractional distillation.

The crude oil was first distilled to 180° from an ordinary distilling flask, in the manner adopted for the first sample. The yield of "180° run" was 44·65%, sp. gr. 0·755 at 22·25° C. The "180° run" was next fractionally distilled through an 8-pear still-head, lagged with Posidonia fibre; the diameter of the bulbs was 2·5 cm., the total height of the condensing column 102 cm., and the rate of distillation 2 drops per second. The results obtained are given below :—

Fractionation of the "180° run."

Temperature	Weight percentage of "180° run"	Weight percentage of crude oil	Specific gravity
60°–90°	11·2	5·0	0·715 at 24°
90°–120°	37·2	16·6	0·744 at 24·5°
120°–150°	31·3	14·0	0·7615 at 25°
above 150°	17·9	8·0	0·7905 at 24°

In a second experiment the percentages of the four fractions obtained were 11·8, 37·4, 27·8, and 21·3.

(b) Weight taken, 875 grams.

Nitration of fractions.

(a) Two portions of 80 grms. of the first fraction (60°—90°) were nitrated in the manner described above; the results indicated that the fractions contained (a) 5·2, (b) 4·5% of benzene, and (a) 84·4, (b) 81·9% of unaltered hydrocarbons. Taking the above results in conjunction with those obtained for the first sample of the oil, it appears that the fraction of b.pt. 60°—90° contains about 5% of aromatic hydrocarbons. Further, the main aromatic component is probably benzene.

(b) Two portions of 160 grms. of the second fraction (90°—120°), upon nitration in the manner already described for this fraction, gave the following results : Toluene, (a) 13·75, (b) 14·1%; unaltered hydrocarbons, (a) 86·25, (b) 85·9%. A review of the whole of the results obtained for this fraction indicates the aromatic content to be approximately 12%.

It is evident from the above data that by redistilling the "170° run" through a fractionating column up to 120° C., it is possible to produce, in a ready manner, a fraction containing about 10% of aromatic hydrocarbons, these being essentially benzene and toluene. Such a possibility lends considerable interest to the oil as a source of aromatic compounds.

An examination of the higher-boiling fractions of this oil is at present in progress, and a further examination—as far as the available material allows—of the lower-boiling fractions described in this communication is also contemplated.

Department of Organic Chemistry,
    University of Sydney.

COMMONWEALTH OF AUSTRALIA

Institute of Science and Industry

BULLETIN No. 14.

An Investigation of the

"MARINE FIBRE"

——— OF ———

POSIDONIA AUSTRALIS

By

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AND

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INTRODUCTION.

Posidonia Fibre, or "Marine Fibre," has been described in Bulletin No. 4 of the Department of Chemistry of South Australia as "the fibrous portion of the leaf sheath of the sea plant *Posidonia australi*, which grows abundantly in the shallow waters around the coasts of South Australia and on other parts of the Australian coast." The method of occurrence, modes of collection, and general properties of the Fibre are fully described in that Bulletin, which records most of the information hitherto available concerning the material.

The object of the present work was to investigate the physical and chemical properties of the Fibre, with a view to determining the purposes for which it is most suitable (1).*

Two samples of the Fibre have been previously submitted to a general chemical examination at the Imperial Institute (2),* but up to the present the physical and structural characteristics of the material appear to have been only cursorily examined. The first sample, examined at the Imperial Institute in 1909, was merely freed from sand and other associated impurities prior to analysis; the second sample, examined in 1911, was washed in fresh water and then dried in the air before analysis. For purposes of comparison the two sets of values obtained for these samples are quoted in the course of this Bulletin.

As a preliminary to the physical and chemical investigations, a botanical examination and description of the Fibre was undertaken by Mr. R. T. Baker, F.L.S., Curator of the Sydney Technological Museum, to whom our cordial thanks are due. Mr. Baker also rendered much assistance in the preparation and description of the plates.

The structural and physical examination was conducted at the Sydney Technological Museum. We have to express our indebtedness to Mr. F. R. Morrison for his assistance with the arduous series of measurements involved; and to Mr. T. C. Roughley for preparing the sections and taking the photographs reproduced in the Bulletin. A number of the later measurements were made by Mr. F. W. Byrne.

The chemical investigations were mainly carried out in the Organic Chemistry Department of the University of Sydney; and we record our grateful acknowledgments for experimental help rendered by Miss M. M Williams, B.Sc., Mr. A. Evans, B.Sc., and Mr. W. J. Kirchner, B.Sc.

A good deal of information has been placed at our disposal by Mr. W. D. Wade, Managing Director of Australian Marine Fibres Ltd. and Posidonia Fibres Ltd., to whom we also express our thanks. In addition, Mr. Wade kindly supplied the samples of Fibre (Plate XIX.) used in the work.

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* The numbers quoted in brackets in the text indicate that a corresponding reference will be found at the end of the Bulletin.

The material had been dredged from a locality about 10 miles north of Port Broughton, South Australia. It had undergone a single washing on the dredge with sea-water; this process was followed by a mechanical separation, while wet, from sand, shells, and other associated impurities; after which the material was dried in hot air, at about 200° F. (93° C.). After reaching us, the samples were freed as far as possible, by careful sorting and shaking, from the remaining extraneous matter; and the resulting "cleaned fibre" was the material used for the determination of the physical characteristics of the crude product.

JOHN READ.
HENRY G. SMITH.

Sydney, April, 1919.

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Posidonia australis, Hook. *f.* (*N.O. Naiadaceæ*).

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Posidonia australis, Hook. *f.* (*N.O. Naiadaceæ*).

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One-third natural size.

An Investigation of the "Marine Fibre" of Posidonia australis.

By

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and

HENRY G. SMITH,

Assistant Curator and Economic Chemist, Sydney Technological Museum.

A.—BOTANICAL.

I.—BOTANICAL CHARACTERISTICS.

1.—General.

This fibrous material has its origin in the leaves and stems of the mono-cotyledonous plant *Posidonia australis*, Hook. *f.* (*N.O. Naiadaceæ*), which so far has been recorded from the foreshores of Western Australia, South Australia, and New South Wales, as well as in Tasmania; but it probably extends around the whole continent. (Plates I. and II.)

The species was systematically described by Hooker (3) and again by Bentham (4).

It is a marine submerged flowering plant, having organs and anatomy corresponding to those of similar representatives of the floral world, and so is hardly correctly described by Green and Frank (5) as " derived from a land plant . . . . which through an incursion of the sea has been submerged for a considerable period." Nor is Marine Fibre the "bast fibres of the plants," as also stated by these authors. It would appear that the enormous beds of the Fibre are due to the covering of the dead bases of the leaves and stems of the plants by drifting sand, which apparently has acted as a preservative, for the material shows only the slightest sign of decay.

2.—Macroscopical.

When originally brought before the commercial world the material was known as " Tickera " fibre.

When seen in the mass it is pale brown in colour, being of a lighter shade and coarser than cocoanut fibre coir, to which it bears a general resemblance.

Although called " fibres " in this condition, each distinct filament is really a complex structural aggregate or bundle of ultimate fibres, just as a piece of string is composed of a number of strands, each of which again is composed of individual, or ultimate fibres.

The fibre bundles, or filaments, of *Posidonia australis* measure up to 8 or 9 inches in length. Scientifically it is incorrect to call them fibres, but commercially such a term can stand, as the distinction is of no moment in an industrial sense.

3.—Microscopical.

The filaments or bundles are composed of ordinary wood fibres, and are true vascular bundles of prosenchymatous cells distinguished as fibres. These bundles differ from the closed bundles of dicotyledons. The latter are characterised by their persistent cambial strips and phloëm, which are absent in the open bundles of *Posidonia australis* and other monocotyledonous plants.

The commercial " fibres " (filaments) are found to occur throughout the stem and leaves of the plant ; they are stouter at the bases of the leaves and stems than towards the free-ends, and it is only those of the leaf base isolated by the natural retting of the sea waves that remain for collection and utilisation.

In the stem they are scattered irregularly amongst the mesophyll aerenchyma, or water tissue, which surrounds the stele, where they are mostly circular in a cross-section. (Plate III.)

In the leaves they are found under the epidermis and below the palisade parenchyma, and a cross-section shows that whilst composed of a number of fibres they exhibit the most varied polygonal shapes. (Plate V.)

In a longitudinal view these bundles are seen to have the individual, or ultimate fibres arranged in several ways, *i.e.*, in most cases they are parallel with each other ; in others they occur in waves, sometimes intertwining ; or, again, they may exhibit interlocking and twisting, as though plaited. Further, in rare instances an individual fibre will be found winding around portions of the bundle. The individual fibres are attached to one another throughout their whole length, long and short ones being arranged indiscriminately.

The commercial " fibre " may therefore be described as a bundle of individual, or ultimate fibres ; and when examined under a microscope it has a striated appearance due to the lines of the individual fibres. (Plates VI. and VII.)

When viewed under a high power, the individual fibres are seen to be elongated and spindle-shaped, with tapering awl-shaped ends. (Plates XII., XIII., XIV., and XV.) Each fibre is wedged tightly between its neighbours, to which it is firmly attached ; and doubtless the very long fibres impart a considerable degree of stability to the group. The walls are of medium thinness (Plate IV.) ; the lumen is wide, varying, of course, with the diameter of the fibre. The walls possess characteristic, narrow slit-shaped pits, in single or double rows, mostly obliquely placed ; this latter disposition generally indicates that the fibres coil spirally around each other This accounts for the string-like appearance, or spiral course, of some of the fibre bundles when seen individually (*supra*) ; and as such a condition imparts strength to a rope or string, the arrangement is also advantageous in this case from a mechanical point of view.

The outer ultimate fibres of each bundle have swellings, or dilations, on their dorsal surface. (Plate VIII.) These dilations average about four to six, or more, per ultimate fibre, according to the length of the latter. The

mean distance between the protuberances is about 0·15 mm., which is too great for them to be termed collectively a serration. They are, as stated above, situated on the back or outer surface of the exterior ultimate fibres (the inner surface being smooth) ; and as this feature occurs in a corresponding position on each fibre surrounding the bundle, a ringed appearance results, which is not unlike the whorls of leaf scales found in *Casuarina* species. The peculiarity is well illustrated in Plates VI. and VII.

It is difficult to explain the function of these swellings. They are exceedingly minute ; but since vascular bundles in the vegetable kingdom are regarded as mechanical elements, perhaps in this case the dilations projecting into the acrenchyma, or mesophyll, assist in supporting the softer parts of the leaf or stem. In addition to this, it is possible that they may also have a perforation or pitted cell at the apex, thus giving another means of communication by which water or other substances necessary in the life-processes of the bundle may be obtained. Somewhat similar peculiarities of obscure significance are recorded by Krabbe (6) as occurring on the bast fibres of certain dicotyledonous plants. These, he states, are often accompanied by the protoplasts which are encased in secondary cellulose layers. Should the feature now described prove to be of identical character, it will be the first record of the kind in monocotyledonous plants.

B.—STRUCTURAL AND PHYSICAL.

II.—DIMENSIONS AND STRUCTURE OF THE POSIDONIA FILAMENT, AND OF THE DERIVED ULTIMATE FIBRES.

1.—Dimensions of the Posidonia Filament.

(i) Length of Staple.

The unbroken " natural fibres " (*i.e.*, filaments or fibre bundles) of *Posidonia australis* examined by us varied from 100 to 170 mm. in length, but these dimensions are not to be taken as limiting values ; the corresponding dimensions quoted by the South Australian observers (2) are, *e.g.*, 50 to 200 mm. The possibility of such variations is evident from Plate II.

The exceptional shortness of staple of this fibrous material is evident from the appended comparative table (7).

TABLE A.—LENGTH OF STAPLE OF VARIOUS FILAMENTS.

				Millimetres.
Cotton	..	..	..	20– 40
Flax ..	..	..	..	200–1,400
Hemp ..	..	..	..	1,000–3,000
Phormium	..	..	..	800–1,100
Jute ..	..	..	..	1,500–3,000
Esparto	..	..	..	100– 400
Posidonia	..	..	..	100– 170
				50– 200

(ii) Diameter.

The diameters of the Posidonia filaments selected for investigation ranged from 0·040 to 0·200 mm. No individual filament examined was of uniform diameter along the whole length. As a rule, the greatest diameter was situated at about 0·5 to 1 cm. from one extremity ; and from this point onwards there was a gradual diminution in thickness, with the occasional occurrence of swellings.

In the majority of cases, the extreme fine end to which the filament tapers appeared to have been broken off.

In making the measurements tabulated below, the filament was adjusted between two strips of glass, the positions to be measured being marked on the upper strip. The best filaments were selected for examination, and the measurements were made at each cm., starting from the thicker end :—

TABLE B.—DIAMETERS OF INDIVIDUAL POSIDONIA FILAMENTS.

Centimetres ..	End.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.
Millimetres	·173	·200	·173	·173	·120	·126	·133	·133	·100	·133	·120	·106	·100	·100	·093	·066		
,,	·160	·160	·160	·126	·120	·086	·086	·073	·073	·066	·073	·073	·060	·046	·040	·026		
,,	·146	·146	·140	·113	·106	·120	·100	·100	·066	·073	·066	·066	·060	·066	·066	·046		
,,	·146	·146	·153	·146	·146	·093	·086	·100	·100	·113	·113	·100	·086	·093	·086	·086	·080	
,,	·140	·120	·120	·093	·093	·093	·106	·086	·073	·093	·060	·080	·080	·060	·060	·060		
,,	·133	·126	·133	·133	·106	·113	·100	·080	·066	·066	·066	·066	·053	·046				
,,	·133	·173	·093	·093	·093	·086	·086	·073	·100	·086	·086	·073	·066	·056	·060	·066	·046	·046
,,	·120	·120	·113	·093	·106	·100	·106	·106	·066	·073	·093	·093	·080	·080	·098	·086	·053	·046
,,	·120	·120	·113	·120	·106	·100	·080	·073	·060	·066	·066	·073	·080	·073	073	·066	·066	
,,	·113	·120	·098	·093	·093	·080	·080	·066	·060	·060	·060	·046						
,,	·106	·120	·100	·080	·080	·073	·073	·066	·060	·060	·053	·046	·046	·040	·033			
,,	·100	·106	·100	·100	·080	·086	·080	·066	·080	·066	·053	·053	·040					
,,	·093	·107	·107	·107	·120	·100	·087	·087	·080	·080	·080	·087	·067					
,,	·093	·086	·106	·106	·100	·080	·086	·093	·080	·086	·093	·080	·067	·067	·060			
,,	·080	·066	·073	·066	·080	·073	·066	·066	·066	·066	·066	·060	·060	·046				
,,	·060	·086	·093	·086	·080	·080	·073	·053	·053	·053	·040							

The relatively coarse staple of the Posidonia filament is shown in the following table : --

TABLE C.—DIAMETERS OF VARIOUS FILAMENTS.

		mm.
Posidonia, upper limit (Table B)	.. ..	0·20
lower limit (Table B)	.. ..	0·04
mean value (Table B)	.. ..	0·088
Posidonia (8), upper limit	.. ..	0·15
lower limit	.. ..	0·02
Cotton, upper limit ..	.. ..	0·037
lower limit (9)	.. .	0·012
upper limit ..	.. ..	0·020
lower limit (10)	. • ..	0·016
Jute, upper limit ..	.. ..	0·10
lower limit ..	.. ..	0·04
mean value (Table F)	.. ..	0·065
Flax (11), upper limit	.. ..	0·255
lower limit ..	.. ..	0·114

2.—Structure of the Posidonia Filament.

The appearance of the " natural fibre " (filament, or fibre bundle) of *Posidonia australis* when viewed under low magnification is well shown in Plates VI. and VII., which are reproductions of photomicrographs taken by reflected light. The filaments had previously been immersed in Schweizer's reagent for two minutes, washed, and mounted in seccotine between two glass slides. The parallel longitudinal ribbed markings and the dark transverse lines correspond, respectively, to the ultimate fibres and the swellings described above (I., 3).

As shown below (XIII., 1) when chlorinated and raised to the boil with sodium sulphite solution, according to the Cross and Bevan process, the Posidonia filament readily disintegrates into short ultimate fibres. A similar structural disintegration is more slowly effected when the filament is treated with chlorine water for several days.

With moist bromine vapour, acting at the ordinary temperature, it was found possible to follow under the microscope the various stages of this structural disintegration. The very interesting observations made in this way indicate that the filament of *Posidonia australis* is a fibre bundle of complex nature, consisting of numerous longitudinally oriented strands (corresponding to the "ribs" in Plate VII.) embedded in a lignocellulose matrix, and thus firmly cemented together. Twisting or crossing of these strands was rarely observed. They are present to the number of 50 or 60, or sometimes more, in the filaments of greatest diameter ; and they consist of ultimate fibres cemented together by their pointed ends.

The cementing material holding together the ends of the ultimate fibres to form the longitudinal strands must apparently be discriminated from the cementing material which serves to bind these strands together to form the filament or fibre bundle. The latter cementing material is more readily attacked by bromine vapour than the former.

When Posidonia filaments are suspended for three or four days in bromine vapour in a closed vessel—perhaps best over bromine water containing an excess of bromine, so that the space above the liquid is constantly saturated with the vapour—the material which cements together the longitudinal strands is so changed that the strands may readily be separated one from the other by placing the filament between a slide and cover-glass and squeezing it with a pushing motion.

The specimens illustrated (Plates VIII., IX., X., and XI.) were prepared for photographic purposes in this manner. From this result it is apparent that the cementing medium which holds together the ultimate fibres into longitudinal strands has resisted the action of the bromine vapour ; and this is the case even after continued treatment for three or four weeks.

The appearance of the strands when thus separated is evident from Plates VIII., IX., X., and XI. That the strands are composed of a continuous series of ultimate fibres is suggested by the fact that the diameters of the strands are those of the ultimate fibres in their broadest part, and that by treating the original filaments with chlorine water the strands undergo practically complete disintegration into individual ultimate fibres, the whole of the cementing material being comparatively readily susceptible to the action of this reagent. This action of chlorine water on the original filaments is illustrated in Plates XII. and XIII.

The ultimate fibres are easily separated from the thicker of the original filaments by boiling with 50 per cent. nitric acid and potassium chlorate (Plate XIV.); but for the more delicate filaments it is necessary to employ the official soda-chlorine method, or to use chlorine water, because in this way the ultimate fibres are not so readily broken (Plate XV.).

3.—Dimensions of the Ultimate Fibre.

The unbroken doubly terminated ultimate fibres of the material worked upon range in length from 0·7 to 2·0 mm., but fibres measuring above 1·5 mm. in length are rarely seen. This is perhaps largely accounted for by the delicacy of the longest ultimate fibres; these always appear to be narrow in comparison with the others, and thus are more easily broken. The diameter in such cases is usually not above 0·01 mm. The broader and more robust doubly-terminated fibres rarely exceed 1·25 mm. in length, and it may be assumed that the majority of the ultimate fibres of *Posidonia australis* do not exceed 1 mm. in length.

As regards diameter, the majority of the ultimate fibres vary from 0·01 to 0·02 mm., but the greater width mentioned is rarely attained. An occasional ultimate fibre will, however, exceed this value; one such can be seen in the centre of Plate XIV.

It may be added that the most robust ultimate fibres are those separated from the thicker end of the original filament.

The structural peculiairties of the ultimate fibres have been described above (I., 3); in this connexion, the protuberances noticeable in the ultimate fibres of Plate VIII. correspond to the transverse rings of Plate VII., shown under a somewhat different magnification.

In the subjoined table the dimensions of the ultimate fibres of Posidonia are compared with those of various standard fibres (12). The length of the filament (Table A) is also included, as being of interest in the consideration of these relationships :—

TABLE D.—DIMENSIONS OF VARIOUS ULTIMATE FIBRES.

Material.			Length of Filament. mm.	Length of Ultimate Fibre. mm.	Diameter of Ultimate Fibre. mm.
Cotton	..	..	20– 40	20 –40	0·012–0·037
Flax	..	..	200–1400	25 –35a	0·015–0·037
Hemp	..	..	1000–3000	15 –20	0·016–0·050
Phormium	..	..	800–1100	5 –15	0·010–0·020
Jute	..	..	1500–3000	1·5– 4	0·020–0·025
Pinewood (tracheids) b	..		..	1 – 3	0·015–0·020
Esparto	..	..	100– 400	0·5– 3	0·010–0·018
Posidonia ..	..	..	100– 170	0·7– 2	0·01 –0·02
			50– 200	0·5– 1·3	0·02 –0·076 (?)

(a) For a first-class flax, 50 mm. or over (13).
(b) The tracheids of Colonial Pine (*Araucaria Cunninghamii*) measure up to 9 mm. in length, and vary from 0·04 to 0·09 mm. in diameter (14).

The first set of data quoted for the Posidonia fibre are the result of our own measurements; the other figures are taken from previous publications on the fibre (2). We have been unable to confirm the value 0·076 mm. (0·003 inch), which has perhaps been quoted in error.

The relative dimensions of the ultimate fibres of jute and Posidonia are apparent from Plates XV. and XVI.

III.—TENSILE STRENGTH, ELASTICITY, AND FLEXIBILITY OF THE POSIDONIA FILAMENT.

1.—Tensile Strength.

The instrument used in measuring the breaking strain and the corresponding extension of Posidonia filaments is depicted in Plate XVII. The clips for holding the filament are visible on the right, in the upper half of the illustration ; they were adjusted at a distance of 4 cm. apart throughout the whole series of determinations. The filament under examination was fastened in one clip at a distance of 3 cm. from its thicker end, the diameter used for calculating having been previously measured at a distance of 5 cm. from the thicker end, i.e., at the point midway between the clips. This position had to be chosen arbitrarily, but certain reasons of convenience influenced the decision, as also the fact that the mean diameter of the filaments coincides approximately with the diameter at the point indicated. (Table B).

The filament, being firmly gripped in both clips, is submitted to a steadily increasing strain by means of carefully regulated hydraulic pressure, the necessary weight having been attached to the long arm. The amount of the strain and of the corresponding extension of the filament are simultaneously indicated on the two scales ; when the rupture occurs the pointer automatically remains stationary until readjusted, so that the necessary readings may be made at leisure.

The results given below are for the first 100 completed tests, the most perfect filaments from a particular sample of crude untreated fibre (Plate XIX.) having been selected, irrespective of diameter. The filaments are arranged in the order of decreasing diameter, and the values for the breaking strain are calculated in kilograms per sq. mm. of cross-section.

TABLE E.—TENSILE STRENGTH AND EXTENSION OF POSIDONIA
FILAMENTS.

Number of Filaments Tested.	Diameter in Milli- metres. Thicker end.	Breaking Strain in Grams.			Breaking Strain Kilograms per Square Millimetre.	Extension in Milli- metres.			Per- centage Exten- sion.
		Mean.	Highest.	Lowest.		Mean.	Highest	Lowest.	
2	0·173	151·87	160·0	143·75	12·17	2·6	2·8	2·4	6·5
3	0·16	140·42	160·0	113·73	24·17	2·5	2·6	2·4	7·33
3	0·146	144·13	153·75	136·25	21·22	2·5	2·6	2·4	6·25
9	0·14	137·34	158·75	83·75	20·22	1·89	2·9	1·2	4·72
9	0·133	145·50	210·0	118·75	25·05	2·49	3·1	1·6	6·22
13	0·12	111·15	185·0	52·5	14·15	1·9	3·2	0·6	4·75
12	0·113	115·41	162·5	67·5	22·96	2·16	3·2	1·4	5·41
14	0·106	101·25	137·5	62·5	24·19	2·16	2·9	1·4	5·41
10	0·10	98·50	125·0	75·0	16·95	1·64	2·3	0·6	4·1
14	0·093	100·98	140·0	52·5	20·09	2·18	2·9	1·4	5·46
7	0·08	89·46	158·75	52·5	21·37	1·86	3·0	0·7	4·65
4	0·06	61·25	71·25	43·75	12·18	2·42	3·4	1·5	6·05
					Mean				Mean
100	..	..	..	..	20·15	..	..	..	5·29

The mean value for the breaking strain of the Posidonia filament, expressed in kilograms per sq. mm. of cross-section, is thus 20·15. No connexion is apparent between the diameter and the mean breaking strain per unit of

cross-section ; of the filaments selected for examination, the greatest average strength was exhibited by those of the mean diameter 0·133 mm., while those of the next degree of fineness (0·12 mm. diameter) were among the weakest of the series. The irregularities observed may be due to the frequent occurrence of flaws in the filaments ; these may be seen under the microscope as dark specks, which possess no regularity of arrangement.

In order to obtain comparative values for jute, similar determinations were made for ten of the most perfect filaments selected from each of two different samples of jute in the Sydney Technological Museum. The results are tabulated below :—

TABLE F.—TENSILE STRENGTH AND EXTENSION OF JUTE FILAMENTS.

Number of Filaments Tested.	Diameter in Milli-metres.	Breaking Strain in Grams.			Breaking Strain Kilograms per Square Millimetre.	Extension in Milli-metres.			Per-centage Exten-sion.
		Mean.	Highest.	Lowest.		Mean.	Highest	Lowest.	
				First Sample.					
2	0·08	91·87	100·0	83·75	18·27	0·35	0·4	0·3	0·88
3	0·073	97·0	120·0	61·0	23·17	0·36	0·6..	0·2	0·9
2	0·07	98·18	126·25	70·0	25·5	0·55	0·6	0·5	1·37
1	0·06	75·0	..	..	26·53	0·20	..	..	0·5
2	0·053	72·5	74·0	71·0	25·81	0·55	0·8	0·3	1·37
10	..	..	..	..	Mean 23·52	..	..	..	Mean 1·04
				Second Sample.					
1	0·10	115·0	..	..	14·64	0·4	..	..	1·0
1	0·093	177·5	..	..	26·13	0·3	..	..	0·75
1	0·086	125·0	..	..	21·52	0·2	..	..	0·50
1	0·08	80·0	..	..	15·91	0·2	..	..	0·50
1	0·053	35·0	..	..	15·86	0·2	..	..	0·50 .
2	0·046	41·75	47·0	36·5	25·12	0·2	..	..	0·50
3	0·04	42·33	46·0	40·0	33·68	0·2	..	..	0·50
10	..	..	..	..	Mean 24·53	..	..	..	Mean 0·58

The tensile strength of jute is thus shown to be somewhat higher than that of Posidonia, while the very marked variation in strength between different filaments is of the same order for both.

The following table (15) shows more fully how the Posidonia filament compares with various standard filaments in regard to tensile strength; the values are given in kilograms per sq. mm., as above :—

TABLE G.—TENSILE STRENGTH OF SOME STANDARD FILAMENTS.

Hemp	.. ..	45·0–78·0
Raw silk	.. ..	44·8
Cotton	.. ..	37·6
Flax	.. ..	35·2
Cocoa-nut fibre	..	29·2

Jute	..	28·7–49·5
(Table F)	..	14·6–33·7
(Table F, mean)	..	24·0
Posidonia (Table E)—		
upper limit	..	25·05
lower limit	..	12·17
mean value	..	20·15
Wool	..	10·9

Thus, of the standard filaments quoted, Posidonia is superior only to wool in tensile strength per unit area of cross-section ; and although the mean value approaches that obtained by us for jute, the Posidonia filament must be characterised as markedly inferior to jute in tensile strength, owing to the prevalence of flaws. In some instances there are flaws which when observed microscopically give the impression that certain of the outer ultimate strands (II., 2) have been attacked in some way ; and this weak point would naturally be the first to succumb to strain in the tensile strength test. It may also be accepted that there are other adventitious circumstances each tending to make Posidonia " fibre " a more difficult material for comparative mechanical tests than such filaments as cotton, &c. Further, referring to structural considerations, an ordinary Posidonia filament composed of 60 ultimate fibre strands, in which the ultimate fibres are cemented together by their ends as well as longitudinally, must contain a very large number of distinct structural units. In the 40 mm. of filament between the clips of the testing machine no less than 4,800 ultimate fibres would be present, assuming 0·5 mm. to be the free length of each ultimate fibre. The structural conditions are therefore much more complex than, e g., in the case of cotton, in which the filament and the ultimate fibre are identical, and in that of flax, in which the structural units (ultimate fibres), like those of cotton, may easily exceed 50 times the length of the Posidonia unit.

Statements have been made (16) that Posidonia Fibre is weakened by the technical drying with hot air, which is usually accomplished at about 200° F. (93° C.), and that a stronger material is obtained by the slower process of air-drying in the sun. Measurements were accordingly made on 30 of the best filaments selected from a specimen of the air-dried material obtained from the same source as the other specimens examined. It should be remarked, however, that the sample as a whole was inferior to some other consignments we have received, as it contained more fragile and broken filaments.

The mean breaking strain observed for the 30 filaments was 15·9 kilograms per sq. mm., as against the mean value 20·15 obtained for 100 filaments dried in hot air (Table E). It appears from this result that no diminution in tensile strength is brought about by drying the "fibre" with hot air, provided, of course, that it is not overheated. The observed discrepancies must therefore be ascribed to other causes, such as differences in location, robustness of growth, &c.

The actual measurements are summarised below :—

TABLE H.—TENSILE STRENGTH AND EXTENSION OF AIR-DRIED POSIDONIA FILAMENTS.

Number of Filaments Tested.	Diameter in Millimetres. Thicker End.	Mean breaking Strain in Grams.	Mean breaking Strain in Kilograms per sq. mm.	Percentage Extension.
12	0·146	118·1	17·4	5·15
5	0·133	128·9	22·2	5·60
11	0·120	87·7	11·2	5·59
2	0·093	86·2	17·2	5·25
			Mean	Mean
30	..	..	15·9	5·39

2.—Elasticity and Flexibility.

Although the crude Posidonia filament is very brittle and breaks readily on rubbing, or even in many cases snaps when bent or twisted into a loop, it possesses a considerable degree of elasticity when subjected to a steady, direct strain. This statement may be verified by stretching the filament between the fingers; it is also borne out by Table E, in which it is shown that the elongation sustained under the breaking strain varies from 4·1 to 7·33 per cent., and averages 5·29 per cent. The corresponding values for jute are much lower, as is evident from Table F, and also from the appended summary of data abstracted from Tables E and F and other sources (17).

TABLE I.—PERCENTAGE ELONGATION OF VARIOUS FILAMENTS UNDER THE BREAKING STRAIN.

Posidonia, upper limit	..	..	..	7·33
lower limit	..	..	..	4·1
mean ..	..	..	..	5·29
Jute (first sample) upper limit		..	..	1·37
lower limit		..	..	0·5
mean ..		..	..	1·04
Jute (second sample) upper limit		..	..	1·0
lower limit		..	..	0·5
mean ..		..	..	0·58
Jute yarn	..	..	..	2·0
Flax yarn	..	..	..	2·5–3·7
Cotton yarn	..	..	..	3·97

In spite of the high position of Posidonia in this list, it exhibits the lack of flexibility characteristic of short-fibred, highly lignified filaments, and thus differs very markedly from the long-fibred and extremely flexible cellulose filaments.

The transverse brittleness is probably due in some measure to the shortness of the ultimate fibres, which are arranged longitudinally, and to the thinness of their walls (but cf. XVIII., 47); the latter feature is manifest in the section of the bundle when magnified 150 diameters (Plate IV.), and is emphasised by a comparison of Plates XV. and XVI.

The exceptional longitudinal elasticity may be ascribed to the longitudinal orientation of the numerous ultimate fibres, each of which is doubtless capable of undergoing a certain amount of displacement in this direction when the composite filament is subjected to strain.

The data quoted above refer to the percentage extension under the breaking strain only. The curves in Plate XVIII. (in which the unbroken lines represent crude Posidonia filaments) show further that the extension commences with a load of 30 to 50 grams, and increases very regularly with a gradually increasing strain, until the breaking point is reached.

IV.—SPECIFIC GRAVITY.

The specific gravity of the cleaned and washed " fibre " was determined pyknometrically ; adhering air-bubbles were removed by placing the pyknometer under a partial vacuum for about a minute : 1·1814 gram of the material displaced 0·8253 gram of water at 19°.

Hence the specific gravity of the washed and air-dried specimen was 1·429.

C.—CHEMICAL.

NOTE.—For the sake of brevity the material under investigation is referred to throughout the chemical section of the work as " the fibre."

" Cleaned fibre " denotes material which has undergone the processes noted in the Introduction.

" Dried " indicates dried at 100° to constant weight.

" Moist " is equivalent to " air-dried."

" Washed " means washed for 10 minutes in a stream of hot tap water and rinsed with distilled water.

All temperatures are given in Centigrade units unless otherwise stated.

V.—MOISTURE.

The cleaned fibre (0·6 to 1 gram) was heated in an air-oven at 100° until the attainment of constant weight. Different samples, examined at various times, gave the following percentage weights of moisture : -

(i) calculated on the weight
of the moist fibre   ..   11·7   12·6   14·9   16·1   17·3   22·7

(ii) calculated on the weight
of the dried fibre   ..   13·25   14·4   17·5   19·2   20·9   29·4

It was found that the water-content of the same sample varied from day to day, in accordance with the humidity of the atmosphere. The dried crude fibre is very hygroscopic. Owing to the nature of the associated inorganic salts, it seemed probable that the hygroscopicity of the fibre might be lessened by fresh water washing. Accordingly, a sample was well washed with hot tap water, rinsed with distilled water, and air-dried ; the water-content of the washed material was then estimated simultaneously with that of a specimen of the unwashed fibre. The percentage losses of weight are given below :—

	Cleaned Fibre.		Washed Fibre.
(i) calculated on the weight of the moist fibre	21·7	..	16·6
(ii) calculated on the weight of the dried fibre	27·7	..	19·9

The amount of moisture retained by the fibre may thus be reduced appreciably by washing it with fresh water. Such treatment also . removes associated inorganic matter to the extent of 6·8 per cent. of the weight of the dried fibre (VIII. and IX.). Taking this factor into account, it may be calculated that a ton of the crude cleaned fibre, if washed with fresh water and air-dried under the atmospheric conditions obtaining in the above experiment, would be reduced in weight to 17½ cwt., a loss equivalent to 12½ per cent. of the weight of the original unwashed fibre. Considerations of this kind may well possess some degree of technical interest.

The effect of exposing the dried specimens of fibre to the air is indicated by the following summary, which shows the gains in weight calculated as percentages of the amounts of moisture originally present :—

| | Length of Exposure. | | | |
	½ hour.	1 hour.	3 hours.	20 hours.
Cleaned fibre	10·3	15·3	28·1	47·9
Washed fibre	11·8	17·0	30·4	51·5

These figures indicate that the washed fibre tends to attain equilibrium with the atmospheric moisture more rapidly than does the unwashed fibre.

The following table shows the percentage amounts of moisture absorbed by the dried fibre after various periods of exposure :—

| | Length of Exposure. | | | |
	½ hour.	1 hour.	3 hours.	20 hours.
Cleaned fibre	2·8	4·2	7·8	13·2
Washed fibre	2·3	3·4	6·0	10·3

The absolute amount of moisture absorbed by the dried unwashed (i.e., cleaned) fibre is thus always greater than that absorbed by the dried washed fibre when exposed under similar conditions.

All the above determinations were carried out in small stoppered weighing bottles, from which the stoppers were removed when it was desired to expose the fibre to the atmosphere. The rate of absorption of moisture by the dried fibre may be greatly accelerated by allowing it to stand in the open ; thus, when exposed in this way for half-an-hour upon a particularly humid day, a sample of the dried unwashed fibre absorbed 90 per cent. of the amount of moisture originally present.

The values quoted in the Imperial Institute Reports (2) are 11·8 per cent. of moisture for the cleaned fibre and 11·8 per cent. for a different sample of the washed fibre ; the calculation was apparently made in each case upon the weight of the moist fibre.

Owing to the varying water-content of the fibre, the results given in this Bulletin, unless otherwise stated, are expressed as percentages calculated for the dried fibre, the amount of water having been determined when necessary upon a blank sample of the fibre weighed out at the same time as the sample used for analysis.

VI.—ASH.

Upon complete ignition the fibre yielded a clean, white ash. The percentage amounts obtained from two samples of the cleaned and dried fibre were 11·0 and 12·6.

The following values are also to be noted :—

(i) 6·1 per cent. for the cleaned fibre and 4·2 per cent. for the washed fibre (2).

(ii) 16·1 per cent. for the crude fibre, reduced by shaking to 11·5 per cent. (18).

The ash was reduced to 3·1 per cent. by washing the cleaned fibre for about ten minutes in a stream of cold fresh water ; and a further reduction to 2·8 per cent. was achieved by washing with hot water in a similar manner. By using hot, dilute acetic acid the ash was reduced to 0·2 per cent. (cf. XV., 2).

The appended analysis of the ash has been given by Smart (18) for a specimen of the cleaned fibre :—

TABLE J.—COMPOSITION OF THE ASH OF POSIDONIA FIBRE

Residue insoluble in 20 per cent. HCl	..		1·65	per cent.
Silica (soluble)	..	..	2·05	,,
Iron and alumina (Al_2O_3, Fe_2O_3)		..	12·75	,,
Lime (CaO)	..	..	51·60	,,
Magnesia (MgO)	..	..	9·05	,,
Potash (K_2O)	..	..	4·78	,.
Chlorine (Cl)	..	..	6·10	,,
Phosphates (P_2O_5)	..	..	1·81	,,
Sulphuric acid (SO_3)	..	..	7·30	,,
Sodium	..	..	..	Present.

VII.—DECOMPOSITION BY HEAT.

The cleaned fibre (about 2 grams) was placed in a 100 c.c. distilling flask, fitted with a thermometer, and attached to a Schiff nitrometer filled with distilled water. The flask was immersed in an oil-bath and maintained at 100° for 30 minutes, while a current of air was passed through it for the purpose of drying the fibre. The air-current was then stopped and the temperature raised gradually, while the volume of the gas collecting in the nitrometer was noted after each rise of 10°.

The point at which an appreciable decomposition of the fibre set in was indicated by a sudden increase in the volume of the liberated gas. By comparing the graphs obtained in two such experiments with that obtained in a control experiment (without fibre) it was apparent that a fairly rapid decomposition of the fibre sets in at about 200° C. (392° F.). This result is of interest in connexion with the use of the fibre as an insulating material (XX., 2). Winterbottom (19) states that the fibre chars at 350° F. and carbonises at 428° F., while combustion sets in at 500° F.

It may be noted that the water in the nitrometer became acid and was rendered turbid by the passage of the gas. The gas obtained by heating the fibre to 280° C. was uninflammable (probably owing to the admixed air), and the charred residue in the flask possessed the characteristic " empyreumatic " odour developed under similar conditions by wood.

VIII.—COLD-WATER WASHING.

The cleaned fibre was washed in four changes of cold distilled water, leaving five minutes each time ; it was then collected on a cloth filter, washed twice with distilled water, and dried at 100° ; 1·1454 grams of fibre, containing 17·3 per cent. of moisture, gave 0·8828 grams of dried product.

Loss of weight, calculated upon the dried unwashed fibre—

(i) Including moisture = 27·7 per cent.

(ii) Excluding moisture = 6·8 ,,

The loss of weight of 6·8 per cent. is evidently due to the washing out from the fibre of soluble inorganic salts. A similar result was achieved by washing the fibre for a few minutes with tap water, followed by a little distilled water.

It is noteworthy that washing the fibre with fresh water increases its inflammability to a marked degree ; upon kindling a well opened sample of the washed fibre from beneath, combustion proceeded throughout the entire mass of the material ; whereas, with a similar sample of the cleaned unwashed fibre, combustion ceased with the removal of the kindling flame.   It appears, therefore, that for certain applications of the fibre, sea-water would be preferable to fresh water as a washing agent.

The removal of associated mineral matter from the fibre is greatly facilitated if it is washed with fresh water and air-dried before being submitted to the final mechanical purification.

IX.—HOT-WATER WASHING.

1. The cleaned fibre was kept in boiling distilled water for five minutes, transferred to a cloth filter, washed with distilled water, and dried at 100° ; 1·6946 grams of fibre, containing 16·1 per cent. of moisture, gave 1·3249 grams of dried product.

Loss of weight, calculated upon the dried unwashed fibre—
      (i) Including moisture = 26·0 per cent.
      (ii) Excluding moisture = 6·8   ,,

2. The cleaned fibre was also kept in boiling distilled water for one hour, and then treated as above ; 1·6027 grams of fibre, containing 16·1 per cent. of moisture, gave 1·2426 grams of dried product.

Loss of weight, calculated upon the dried unwashed fibre—
      (i) Including moisture = 26·8 per cent.
      (ii) Excluding moisture= 7·7   ,,

A short treatment with boiling water is thus equivalent to a longer treatment with cold water.   Prolonged contact with boiling water appears to affect the fibre-substance to a slight extent, as indicated by the last value ; in this case the water acquired a pale-yellow colour and the fibre was cleaner, but no other alteration was apparent.

X.—ALKALINE HYDROLYSIS.

1. The cleaned fibre was kept in a boiling 1 per cent. solution of sodium hydroxide for five minutes, after which it was transferred to a cloth filter and well washed—first with distilled water, then with a little dilute acetic acid, and finally again with distilled water.   The bulk of the adhering water was squeezed out, and the fibre opened out on a paper tray to dry ; the drying was eventually completed at 100°, before weighing ; 2·0717 grams of fibre, containing 16·1 per cent. of moisture, gave 1·5705 grams of dried product. .

Loss of weight, calculated upon the dried fibre—
      (i) Unwashed = 9·6 per cent.
      (ii) Washed   = 3·05   ,,

2. The fibre was kept in a boiling 1 per cent. solution of sodium hydroxide at constant volume for one hour, and then treated as above ; 1·7934 grams of fibre, containing 16·1 per cent. of moisture, gave 1·3142 grams of dried product.

Loss of weight, calculated upon the dried fibre :—
      (i) Unwashed = 12·7 per cent.
      (ii) Washed   = 6·3   ,,

The α– and β– hydrolysis values for the washed and dried fibre are thus 3·05 and 6·3 respectively. The following summary gives the values which have been obtained for various samples of Posidonia fibre (2) ; and corresponding values for jute (20) have been added, for purposes of comparison :—

	Imp. Inst. No. 1.	Imp. Inst. No. 2.	Present sample.	Jute.
α-hydrolysis, loss per cent.	0·1	Nil	3·05	13·3
β-hydrolysis, loss per cent.	1·9	1·5	6·3	18·6

These figures demonstrate the exceptional resistance offered by the fibre to alkaline agents (21), a property in consonance with the stability exhibited by it towards other fibre reagents (XIV., 7).

During the boiling with dilute alkali the solution acquired an intense yellow tinge, and the fibre was stained a golden yellow.

XI.—ACID PURIFICATION.

The cleaned fibre was placed in 20 per cent. acetic acid, which was slowly raised to the boil. The fibre was then removed and washed with water and alcohol ; it was finally dried at 100° and weighed—1·2818 grams of fibre, containing 17·3 per cent. of moisture, gave 0·9084 grams of dried product.

Loss of weight, calculated upon the dried fibre —

    (i) Unwashed := 14·3 per cent.

    (ii) Washed   == 8·0   ,,

Of the 8·0 per cent. loss suffered by the washed fibre, 2·6 per cent. is due to loss of inorganic material (VI.) ; so that the loss of fibre-substance is only 5·4 per cent., calculated on the washed and dried fibre.

Winterbottom (22) states that samples of the fibre washed with sea-water and cleaned by the dry process gave acid purification losses of 15 to 25 per cent., while after fresh-water washing and wet cleaning the loss was only 5 to 8 per cent. It will be noticed that these figures are in agreement with the above results. The values obtained for the samples examined at the Imperial Institute were 7·8 and 4·6 per cent.

It has been estimated that a fresh-water washed fibre, showing an acid purification loss of from 5 to 8 per cent., could be prepared and landed at a European port at a cost of £19 per ton (23).

XII.—MERCERISATION.

The cleaned fibre was left in contact with a 33 per cent. solution of sodium hydroxide for one hour, and after thorough washing with distilled water was dried at 100° ; 1·3273 grams of fibre, containing 17·3 per cent. of moisture, yielded 0·9922 gram of product.

Loss of weight, calculated upon the dried fibre—

    (i) Unwashed == 9·6 per cent.

    (ii) Washed   == 3·0   ,,

Filaments which have been submitted to this treatment are characterised by their pale-yellow colour, pronounced lustre, and distinctly wavy outline. The small percentage loss of weight again illustrates the stability of the fibre towards certain reagents which affect other classes of vegetable fibres to a marked extent—thus, under similar conditions to the above, jute is stated to undergo a loss of 11 per cent. (20).

XIII.—POSIDONIA CELLULOSE.

1.—Estimation.

(i) In accordance with the standard modification of the Cross and Bevan process (24), the cleaned and dried fibre was boiled with 1 per cent. sodium hydroxide solution for 30 minutes before chlorination ; exposure to the action of the halogen being in all cases continued for one hour after the initial rapid absorption had ceased. Treated thus, and subsequently submitted in the usual way to the action of alkaline sodium sulphite solution, 4·4440 grams of the unwashed fibre, dried at 100°, gave 2·1198 grams of cellulose, dried at 100° ; cellulose = 47·7 per cent.

A similar determination gave the value 50·5 per cent. for a second sample of fibre from the same bundle.

The mean value, 49·1, when corrected for water-soluble material (IX., 1) and ash (VI.), gives a percentage cellulose-content for the actual fibre-material of 54·2.

(ii) More satisfactory results were obtained by using well washed and air-dried samples of the fibre, and carrying out a parallel determination of moisture and ash—3·9810 grams of fibre, containing 18·1 per cent. of moisture (calculated upon the air-dried fibre) and 2·82 per cent. of ash (calculated on the fibre dried at 100°), yielded 1·7576 grams of cellulose dried at 100° ; and 3·9298 grams of the same sample yielded 1·7325 grams of cellulose. The percentages of cellulose given by the actual fibre-material are thus 55·5 and 55·4 per cent. respectively.

(iii) In view of the woody nature of the fibre, it was considered advisable to estimate the cellulose after a preliminary boiling for one hour with 1 per cent. sodium hydroxide. In this case, 1·1477 grams of the unwashed, air-dried fibre, containing 22·7 per cent. of moisture, yielded 0·4103 gram of cellulose, dried at 100°. From this result, the unwashed fibre, dried at 100°, would contain 46·3 per cent. ; the washed (IX., 1) and dried fibre, 49·6 per cent. ; and the pure, ashless fibre-material, 51·0 per cent. of cellulose.

(iv) The above values for the cellulose-content are appreciably lower than those quoted in the Imperial Institute reports, viz., 55·9 per cent. for the mechanically cleaned fibre, and 63·6 per cent. for a washed sample. It appears, however, that in these determinations the preliminary boiling with 1 per cent. sodium hydroxide was limited to 5 minutes (25).

A determination which was carried out by us in this manner resulted as follows :—3·7288 grams of unwashed, air-dried fibre, containing 16·1 per cent. of moisture, yielded 2·2613 grams of cellulose, dried at 100°. The very high values of 72·3, 77·6, and 79·9 per cent. of cellulose are thus obtained for the dried unwashed fibre, the dried washed fibre, and the ashless fibre-material respectively. The product was dark-brown in colour, and retained the general characteristics of the original fibre ; the natural filaments remained to a large extent intact, and the process was obviously incomplete.

(v) Reviewing the above results, it appears likely that the cellulose-content of the pure ashless fibre-material under examination approximated very closely to 55 per cent.

The average percentage amounts of cellulose yielded by jute (26), Posidonia fibre, woods (27), and straws (28) are summarised below :—

TABLE K.—PERCENTAGE YIELDS OF CELLULOSE FROM VARIOUS SOURCES.

Jute 70 ..	Posidonia 55 ..	Pine 57 ...	Straws 46·5
to		Birch 55·5	to
80		Fir 53·3	53·5
		Beech 45·5	
		Oak 39·5	

It may be observed that when brought into the atmosphere of chlorine the fibre assumed a bright orange colour, which was changed to brown by the alkaline sulphite solution ; the latter colour was also retained by the cellulose. The cellulose obtained by methods (i) and (ii) was a pale-brown mass of felted fibres, closely resembling some of the cruder forms of paper in texture and appearance. The natural filaments were almost entirely disintegrated into " ultimate fibres " during the process of isolating the cellulose. In order to render such disintegration absolutely complete, a more prolonged treatment was necessary, the yield of cellulose being then correspondingly lower. The cellulose was readily bleached to a light-cream colour by treatment with 0·1 per cent. potassium permanganate solution, followed by sulphurous acid.

2.—Chemical Properties.

(i) Action of Fehling's Solution.

The cellulose obtained by the above methods reduced Fehling's solution only very slightly at the boiling-point ; the cellulose developed a yellow colour during the process.

(ii) Action of Concentrated Sulphuric Acid.

It dissolved readily in cold concentrated sulphuric acid, giving a pale-brown solution which gradually darkened and became opaque ; a clear, faintly yellow liquid resulted on pouring this solution into water. On boiling the aqueous solution for a short time and adding a slight excess of sodium hydroxide, an intense yellow tinge was produced, and the hot alkaline liquid reduced Fehling's solution markedly. The products of resolution, which should be of considerable interest, have not yet been investigated.

(iii) Hygroscopic Moisture and Ash.

The hygroscopic moisture, or water of condition, of the air-dried cellulose was estimated at 10·1 per cent. (calculated on the air-dried material), and the ash at 0·1 per cent. (calculated on the cellulose dried at 100°).

(iv) Furfural Value.

By distilling the air-dried cellulose with 12 per cent. hydrochloric acid and precipitating as phloroglucide (29), the yields of furfural obtained in a duplicate determination amounted to 9·18 and 9·23 per cent., respectively, calculated upon the pure dry cellulose. The following list shows how Posidonia cellulose compares with other celluloses in this respect :—

TABLE L.—FURFURAL VALUES OF VARIOUS CELLULOSES.

	Percentage of Furfural.
Woods (coniferous) (30)	2 to 3
Woods (general) (31)	2 to 6
Jute (32)	4 to 5
Posidonia	9·2
Straws and Esparto (30)	12 to 13

(v) Action of Aniline and of Phloroglucinol.

Posidonia cellulose develops no colour when heated with acid solutions of aniline or phloroglucinol.

(vi) Nitration.

Specimens of Posidonia cellulose (XIII, 1, ii) were nitrated for one hour at the ordinary temperature in a mixture of equal volumes of concentrated nitric acid (sp. gr. 1·42) and concentrated sulphuric acid (sp. gr. 1·84). The product was drained, washed thoroughly with cold and hot water, and dried at 100° (25); 1·5138 grams of the dried cellulose gave 2·0285 grams of nitrated product; and 1·5070 grams of the dried cellulose gave 2·0050 grams of nitrated product. Hence, the mean yield, calculated upon the weight of dried cellulose, was 133·5 per cent.

The product, which contained 10·03 per cent. of nitrogen (estimated by the Lunge nitrometer), was only slightly coloured, and it possessed the rough feel characteristic of nitrated celluloses. Instead of remaining distinct, as in the case of nitrated Posidonia fibre (XV.), the fibres of nitrated Posidonia cellulose tended to form small felted aggregates. Ignition occurred with great rapidity, and the residue was insignificant. Gelatinisation with alcohol-ether was practically as complete as in the case of nitrated cotton wool prepared under similar conditions.

Cotton-wool, when nitrated in a similar manner, gave a yield of 169·5 per cent. (XV., 1, iv).

By nitrating Posidonia cellulose for sixteen hours in a mixture of three parts by weight of concentrated sulphuric acid (sp. gr. 1·84) and one part of fuming nitric acid (sp. gr. 1·5), the yield of nitrated cellulose obtained was practically the same as with the weaker nitrating acid, viz., 133·8 per cent. The product contained only 11·51 per cent. of nitrogen. These low values may perhaps be attributed to the pronounced chemical reactivity of certain of the cellulose components (XIII., 3), and their consequent disintegration in presence of the strong nitrating acid. It may be remarked that some of the specimens of the higher nitrate proved to be so unstable as to decompose with explosive violence during the drying operation.

(vii) Preparation of Viscose.

When mercerised with strong sodium hydroxide solution for two days, a pale yellow alkali-cellulose was obtained, which upon treatment in the usual way (33) with carbon disulphide and water yielded a pale-brown viscose.

Satisfactory cellulose films were prepared from such laboratory specimens of Posidonia viscose.

3.—Varieties of Posidonia Cellulose.

(i) In attempting to free the fibre from inorganic matter and incidental impurities, recourse was had, among other methods, to boiling the fibre with dilute sulphuric acid. Two samples of the washed fibre, which had been dried at 100°, were boiled for three hours at constant volume with 3 per cent. sulphuric acid; 5·6949 grams gave 3·5812 grams of product, and 5·1920 grams gave 3·2330 grams of product, dried at 100°. The two samples thus underwent respective losses in weight of 37·1 and 37·7 per cent.; and, taking into account the presence of 2·8 and 0·7 per cent. of ash in the original

and the treated fibre, respectively, the mean loss of actual fibre-material was 36·3 per cent. The product consisted of a mass of brown, brittle filaments, averaging not more than 0·5 cm. in length. In each case the acid liquor when neutralised reduced Fehling's solution markedly.
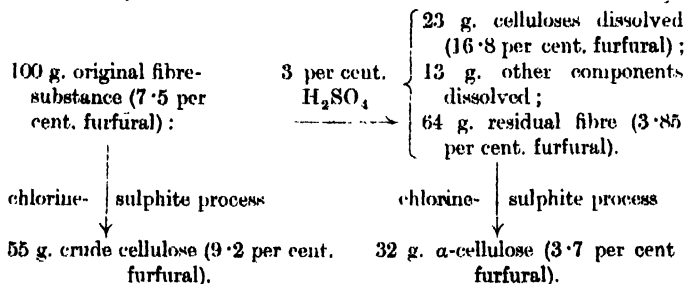
A second treatment of the residual fibre with a fresh quantity of acid for a further period of three hours resulted in no further appreciable loss of weight, and the liquor exerted no reducing action upon Fehling's solution. In a particular case the total loss after the double treatment amounted to 35·7 per cent., calculated for the fibre-material, as above. It appears, therefore, that the fibre-material undergoes a fairly constant loss of about 36 per cent. when boiled for three hours or more with 3 per cent. sulphuric acid.

The residual fibre, when distilled with 12 per cent. hydrochloric acid in the usual manner, yielded 3·85 per cent. of furfural, corresponding only to 33 per cent. of the furfuroids of the original fibre (XIV., 5).

The yield of cellulose, isolated by the standard method (XIII., 1, ii), amounted to very nearly 50 per cent., calculated on the pure fibre-material; 3·2330 grams of residual fibre, containing 0·7 per cent. of ash, gave 1·6000 grams of cellulose, dried at 100°. That this cellulose was not identical with that obtained directly from the fibre (XIII., 1, i and ii) is at once evident from the fact that it yielded only 3·7 per cent. of furfural (cf. XIII., 2, iv).

The cellulose prepared in this way represents only 58 per cent. of that obtained from the original fibre by the direct process ; its furfural constant is much lower; and, although changed to a dull brown colour when boiled with Fehling's solution, it effects no appreciable reduction : it may therefore be regarded as a resistant α-cellulose. Further, postulating that the furfuroid complexes of the α-cellulose have undergone no alteration under the influence of the sulphuric acid and that none of the α-cellulose has been lost, the original cellulose (obtained in 55 per cent. yield from the fibre, and corresponding to 9·2 per cent. of furfural) may be regarded as consisting of 58 per cent of α-cellulose, yielding 3·7 per cent. of furfural, and 42 per cent. of other celluloses, corresponding to 16·8 per cent. of furfural.

The relationships concerned are summarised below : -

100 g. original fibre-substance (7·5 per cent. furfural) :

3 per cent. H₂SO₄ →

- 23 g. celluloses dissolved (16·8 per cent. furfural) ;
- 13 g. other components dissolved ;
- 64 g. residual fibre (3·85 per cent. furfural).

chlorine- | sulphite process
↓
55 g. crude cellulose (9·2 per cent. furfural).

chlorine- | sulphite process
↓
32 g. α-cellulose (3·7 per cent furfural).

(ii) The results just reviewed were supplemented by an examination of Posidonia cellulose obtained directly from the fibre (XIII., 1, ii). When macerated for half-an-hour with 17·5 per cent. sodium hydroxide solution,

according to the method described by Cross and Bevan (31), the material was resolved into a resistant α-cellulose, insoluble in alkali; a β-cellulose, which was precipitated from the filtrate on the addition of acid; and a γ-cellulose, which remained in the acid solution. The percentage yields, corrected for loss of weight at 100° and for the ash of the original cellulose (0·1 per cent.), are appended. The water-content and furfural values are also recorded :—

TABLE M.—COMPOSITION OF CRUDE POSIDONIA CELLULOSE.

Material.	Percentage Amounts (dried at 100°).	Loss of Weight at 100°.	Furfural Value.
Crude Posidonia cellulose	100	10 per cent.	9·2
α-Posidonia cellulose	79·2	13 ,,	2·9
β-Posidonia cellulose	5·3	..	..
γ-Posidonia cellulose	15·5 (diff.)	..	28·9

The yield of resistant α-cellulose, calculated on the weight of the original fibre-substance (43·6 per cent.) is thus markedly higher than that obtained by the first method described (32 per cent.). When the lower furfural value of the second product is also taken into account, the second method of resolution appears to be preferable to the first. It is noteworthy, however, that the resolving action of the caustic alkali upon these celluloses is indeterminate, depending upon the time of contact, &c. (34); whereas the action of dilute sulphuric acid on the fibre-substance seems to be well defined. A more detailed investigation of these relationships seems to be desirable in connexion with the study of the cellulose chemistry.

The action of caustic alkali upon the α-cellulose possessing the higher furfural value (3·7 per cent.), which is also a point of interest, was not examined, as a further characterisation of these products was considered to be beyond the scope of the present investigation. It is hoped, however, that the work may be extended at a later date.

In connexion with the aspect of the subject under review, the following summary is of interest as revealing a decided chemical similarity between Posidonia cellulose and Esparto cellulose :—

TABLE N.—A CHEMICAL COMPARISON OF POSIDONIA AND ESPARTO CELLULOSES.

Material.	Posidonia Cellulose.		Esparto Cellulose (35).	
	Proportion per cent.	Furfural Value.	Proportion per cent.	Furfural Value.
Crude cellulose	100	9·2	100	12·5
α-cellulose	79·2	2·9	84·1	4·0
β-cellulose	5·3	..	..	..
γ-cellulose	15·5	28·9	15·9	26·0

4.—Summary.

The chemical behaviour of Posidonia cellulose shows that it differs markedly from the " normal " cellulose of cotton, flax, &c., and that it partakes rather of the nature of an oxycellulose (36), thus resembling the cellulose from

jute, and, more closely, the celluloses from cereal straws and esparto. The data summarised in the following classificatory scheme for the fibrous celluloses (30) may be quoted in order to illustrate the relationships concerned :—

TABLE O.—CLASSIFICATION OF THE FIBROUS CELLULOSES.

Material.	Furfural per cent.	Fehling's Solution
(a) Cotton, flax, hemp	0·2– 0·5	No reduction
(b) Wood (coniferous)	2·0– 3·0	Slight reduction
(c) Esparto, straw	12 0–13·0	Considerable reduction
Posidonia	9·2	Slight reduction

Posidonia cellulose would thus appear to differ chemically from the usual celluloses obtained from woods and lignified tissues, which yield from 2 to 6 per cent. of furfural (31), and to occupy an intermediate position between these celluloses and those of the straws and esparto, inclining to the latter class. Posidonia cellulose, however, may be discriminated very readily from the straw and esparto celluloses through the fact that whereas these celluloses give a rose-red colouration with a hot solution of an aniline salt, Posidonia cellulose develops no colour (or, at the most, a faint-yellow tinge) with the reagent.

The distinction between Posidonia cellulose and " normal " cellulose is further strikingly illustrated by the results of nitration experiments—cotton-wool gives a much higher yield than Posidonia cellulose, and the two products exhibit a very great difference in stability.

5.—Posidonia Cellulose as a Paper-making Material.

The question of the utilization of the fibre in the paper-making industry has been investigated and discussed by Hargreaves (37) and Earl (38), who conclude that Posidonia cellulose would be a suitable material for that purpose, provided only that certain economic conditions could be fulfilled. In the first place, the cost of production of the fibre would have to be reduced to £4 per ton, or less ; and, secondly, since the chemical behaviour of the fibre points to chlorine as the most effective resolving agent, a cheap supply of that element would be needed. The Kellner electrolytic process for isolating cellulose, in which the chlorine is produced by the electrolysis of brine, has therefore been suggested as the most suitable in the case of Posidonia fibre.

As regards the present investigation, it is indicated below (XVII., 2, vi) that in structure and dimensions the ultimate fibre of Posidonia resembles other fibres which are used extensively in paper-making. The flexibility of the fibre, and its felting properties, &c., are likewise distinctly favorable factors for this general purpose. Further, it is of interest that the chemical characteristics of Posidonia cellulose, in particular the high furfural value, point to its suitability as a material for the manufacture more especially of printing paper and the lower grades of writing papers (39).

Whether the peculiar association of properties encountered in the Posidonia fibre would fit it pre-eminently, either alone or in admixture with other types of fibre, for the achievement of any special purpose in the paper-making industry, is a matter for technological opinion and research (cf. XX., 5). One peculiarity may, however, be mentioned in this place. Although emphasis has been laid upon the importance of straw as an Australian raw material for use in paper-making (40), it should be noted that Posidonia cellulose is not coloured by solutions of aromatic amines (XIII., 2, v); whereas the reactivity of straw and esparto celluloses towards such reagents may be regarded as a marked defect of these paper-making materials (41).

XIV.—CHEMICAL NATURE OF POSIDONIA FIBRE.
1.—Colour Reactions.

In previous investigations of Posidonia fibre attention has been directed to its chemical similarity to jute (2), which is regarded by Cross and Bevan as the chemical prototype of the substance of lignified tissues (42). Although various chemical tests when applied to Posidonia fibre yield results broadly analogous to those recorded for jute, yet in most cases it is possible to establish a definite distinction between the two materials.

Thus, the specific colour reactions are usually more intense for Posidonia than for jute, as is evident from the following results of a series of comparative tests carried out on samples of the two materials :—

TABLE P.—COLOUR REACTIONS OF JUTE AND POSIDONIA FIBRE.

Reagent.	Colour	
	Jute.	Posidonia.
Aniline hydrochloride	Pale yellow	Deep golden yellow
p-Nitraniline hydrochloride	Lem n yellow	I itense ora ige red
Dimethyl-p-phenylenediamine sulphate	Intense purple	In e ise purple
Phloroglucinol in HCl	Pale magenta	Deep magenta
Ferric ferricyanide	Deep blue	Very deep blu
Chlorine	Bright yellow	Bright orange
Chlorine followed by sodium sulphite	Magenta red	Brown

. The reducing action exerted upon ferric ferricyanide is pronounced, and a considerable amount of pigment is absorbed. Like jute, the fibre absorbs iodine from a dilute solution in potassium iodide, thereby assuming a golden-brown colour. When steeped in silver nitrate solution the fibre is stained a greyish colour, owing apparently to reduction of the reagent. Cochineal tincture has little effect upon the fibre. Colourless magenta colours it pink. Concentrated nitric acid produces a colour ranging from golden-brown to dark-brown.

The above colour reactions clearly resemble those of the woods ; and it appears that Posidonia fibre is less saturated and more reactive than jute, and thus corresponds to a higher proportion of lignone. Further evidence in support of this view is adduced in the sequel.

2.—Phloroglucinol Value.

In the case of phloroglucinol the colour reaction was traced quantitatively by submitting the fibre to the action of a measured excess of phloroglucinol in presence of hydrochloric acid and titrating back with a standardised formaldehyde solution, according to the method described by Cross, Bevan, and Briggs (43). The phloroglucinol absorption values obtained as the result of a determination carried out in duplicate upon the fibre were 8·57 and 8·37 ; these numbers denote the quantity of phloroglucinol reacting with the lignocellulose, expressed as a percentage on a sample of the washed and dried fibre yielding 2·8 per cent. of ash. The mean value for the pure ashless fibre is thus 8·71. The values obtained by the above investigators for various related materials are appended for purposes of comparison :—

TABLE Q. —PHLOROGLUCINOL VALUES OF SOME LIGNOCELLULOSES.

Jute (best).	Jute (ordinary).	Mechanical Wood-pulp.	Posidonia Fibre.
3·98	4·23	6·71	8·71

Assuming (44) the ratio lignone : phloroglucinol = 100 : 23·2, the above result corresponds to 37·5 per cent. of lignone for Posidonia fibre. Although the numerical expression is to be accepted with caution, it is evident that the chemical characteristics of the material under examination are those of an exceptionally highly lignified cellulose.

3.—Methyl Value.

A certain amount of light is thrown upon the composition of lignified tissues by applying the Zeisel method for the determination of methoxyl, the " methyl value " for " pure lignin " being taken as 52·9 (45).

In the case of Posidonia fibre, a specimen which had been purified with hot 20 per cent. acetic acid (XI.) gave 4·45 per cent. of methoxyl, as a mean of three concordant results, after allowing for moisture (10·5 per cent) and ash (0·2 per cent.). The corresponding value for jute (46) is 4·6 per cent., and for beech (47) 6·0 per cent.

The methyl value for the pure fibre-substance is thus 21·6, corresponding, according to the above convention, to 40·8 per cent. of lignin. The methyl value 21·20, corresponding to 40·26 per cent. of lignin, has been quoted for jute (48).

Posidonia cellulose, prepared as described above (XIII., 1, ii), yielded only 0·13 per cent. of methoxyl, this value being the mean of three concordant results, corrected for moisture (7·8 per cent.) and ash (0·1 per cent.). The methoxyl groups of Posidonia lignocellulose, like those of jute lignocellulose (46), are thus associated with the lignone complex.

4.—Elementary Composition.

The amounts of carbon and hydrogen in the fibre were estimated according to Liebig's method, the samples having been thoroughly washed, and dried at 100°, prior to combustion. The mean values, derived from a series of

four determinations, were 46·62 per cent. of carbon and 5·73 per cent. of hydrogen ; and as the dried fibre contained 2·82 per cent. of ash, the corrected values are as below –

$$C = 48·0 \text{ per cent.}$$
$$H = 5·8 \quad,,$$
$$O \text{ (diff.)} = 46·2 \quad,,$$

The high percentage of carbon is consonant with the inclusion of the fibre in the lignocellulose group, the following carbon percentages being quoted by Matthews (20) :—

Cotton Cellulose.	Pectocelluloses.	Lignocelluloses.
44·4	40 to 43	45 to 50

Accepting the value C = 47·08 per cent. for purified jute, Cross (49) indicates that the relative amounts of lignone (C = 57·8 per cent.) and cellulose (C = 44·4 per cent.) are 20 per cent. and 80 per cent., respectively. The corresponding values obtained from the above analysis of Posidonia fibre are, approximately, 30 per cent. and 70 per cent.

In connexion with the position of the fibre in the group of lignocelluloses, the following figures (50) are of interest :—

	Jute.	Posidonia.	Beech.
Carbon per cent.	46·5 to 47·0	48·0	49·1*

5.—Furfural Value.

Two samples of the washed and air-dried fibre when distilled with 12 per cent. hydrochloric acid yielded, respectively, 7·53 and 7·42 per cent. of furfural, estimated in the manner indicated above (XIII., 2, iv) and calculated upon the weight of the dry, ashless fibre. The mean value is thus less than the corresponding value for either jute (32) or beech-wood (47) :—

TABLE R.—FURFURAL VALUES OF SOME LIGNOCELLULOSES.

	Posidonia Fibre.	Jute Fibre.	Beech-wood.
Furfural per cent.	7·5	8 to 9	12·8

The value 9·2 obtained for Posidonia cellulose (XIII., 2, iv) corresponds only to 5·1 per cent. calculated upon the weight of the original fibre from which the cellulose was prepared ; so that the remaining 2·4 per cent. of furfural is produced from furfural-yielding groups which disappear during the isolation of the cellulose. From these data it appears that about 68 per cent. of the furfuroids are conserved in Posidonia cellulose, as against 50 per cent. in the case of jute (51).

The curious fact is thus revealed that, although Posidonia fibre yields somewhat less furfural than jute fibre, yet Posidonia cellulose yields about twice as much furfural as does jute cellulose (Table L). A noteworthy distinction exists therefore between these two varieties of lignocellulose.

6.—Action of Halogens.

A very pronounced chemical characteristic of the fibre is its susceptibility to the halogen elements, particularly to chlorine. The structural disintegration produced by chlorine and bromine has already been described (II., 2) ; chemically, the action of chlorine is of particular interest as affording the best means of isolating the fibre-cellulose (XIII., 1).

Chlorine is absorbed by the moist fibre, especially after a short boiling with 1 per cent. sodium hydroxide, with remarkable avidity and completeness. The absorption is effected with such ease that the fibre might well be used, in conjunction with alkali, as a filling for respirators designed for use in a chlorine-laden atmosphere. The volume of chlorine disappearing in the chlorination of the fibre is large, and hydrochloric acid is produced to a marked extent during the process.

It is stated by Cross and Bevan (52) that in the case of jute about one-half of the disappearing chlorine (which amounts to about 16 or 17 per cent. of the weight of the fibre) is eliminated as hydrogen chloride : from which it is concluded that with jute the reaction is one of simple replacement of hydrogen by chlorine, although in the case of other lignocelluloses it is indicated that oxidative processes may occur simultaneously.

Repeated attempts were made to determine the volume of chlorine which disappears in the chlorination of Posidonia fibre ; but neither by the use of Cross and Bevan's original apparatus (53) nor by the employment of the Lunge nitrometer could concordant results be obtained. Control experiments showed a gradual and indefinitely prolonged absorption of chlorine, in the absence of the fibre, under the conditions prescribed ; and as it was not found possible to deduce any satisfactory correction from the control experiments, the determination was at length abandoned. The results indicated that the amount of chlorine reacting with Posidonia fibre is of the same order as the amount quoted by Cross and Bevan for jute.

7.—Behaviour towards other Reagents.

Posidonia fibre resists the solvent action of such cellulose reagents as zinc chloride solution, the Schweizer reagent (cf. XVIII., 12), caustic soda solutions, &c. (X. and XII.) : in these particulars it differs from the lignocelluloses of the jute type and resembles the woods, and, to a lesser extent, the cereal straws.

When left in contact with strong sodium hydroxide solution for several days and then exposed to the action of carbon disulphide vapour, partial gelatinisation occurred (cf. XIII., 2, vii). The woods are unaffected by such treatment (47).

8.—Summary.

The chemical behaviour of Posidonia fibre corresponds to that of a reactive lignocellulose intermediate in character between jute lignocellulose and wood lignocellulose, although the derived cellulose appears to be more closely related to straw and esparto celluloses than to those of jute or woods (XIII., 4). Posidonia fibre, although more reactive and less saturated than jute, as illustrated, e.g., by the phloroglucinol reaction (XIV., 2), is in many respects more resistant than jute towards chemical influences, and this is particularly the case with alkaline reagents (X. and XII.).

The proportion of lignone in the case of Posidonia fibre probably amounts to about 40 per cent., as compared with 30 per cent. for jute.

In contrast to the usual monocotyledonous fibre-aggregates, such as phormium, aloe fibres, esparto, and bamboo, Posidonia fibre appears to consist solely of lignocellulose, rather than of lignocellulose associated with pecto-cellulose. The absence of the latter may be due to the retting action of sea-water on the original material.

XV.—NITRATION OF POSIDONIA FIBRE.

1.—Partial Nitration.

The nitrations described below were effected by immersing the fibre, for a period of one hour at the ordinary temperature, in a mixture of equal volumes of concentrated nitric acid (sp. gr. 1·42) and concentrated sulphuric acid (sp. gr. 1·84). The product was drained and immersed in a large volume of distilled water; after a subsequent washing with cold water, it was heated to the boiling point with a fresh quantity of water, and finally dried at 100° (25).

(i) A sample of the cleaned, unwashed fibre, weighing 1·3236 grams and containing 14·9 per cent. of moisture, gave 0·9700 gram of nitrated product.

Loss of weight, calculated upon the dried fibre—

Unwashed = 13·9 per cent.
Washed = 7·6 ,,

Imperial Institute value (2), 7·0 per cent. gain.

The product consisted of soft, brittle " fibres," much shorter than the original filaments, and possessing a pale-yellow colour, in agreement with the lignified nature of the raw material. A brownish-yellow colour was imparted to the nitrating acid. The product contained 9·30 per cent. of nitrogen; it burnt rapidly, with the deposition of a considerable amount of a black residue. In contact with alcohol-ether it gelatinised to some extent, leaving, however, a large residue of hard fibrous material.

(ii) A dried specimen of the fibre which had been boiled in 1 per cent. sodium hydroxide for one hour was nitrated in the same manner; 1·2894 grams yielded 1·2294 grams of nitrated product.

Loss of weight, calculated upon the prepared fibre = 4·65 per cent.
Loss of weight, calculated upon the unwashed = 16·8 ,,
    original fibre (dried)
Loss of weight, calculated upon the washed = 10·7 ,,
    original fibre (dried)

The product resembled that obtained from the crude fibre, except that somewhat less ash was produced upon ignition. After keeping for several months it decomposed rapidly when heated to about 85°.

(iii) A dried specimen of the fibre which had been submitted to a preliminary boiling for three hours at constant volume with 3 per cent. sulphuric acid was also nitrated similarly; 1·3284 grams of the prepared fibre gave 1·5376 grams of nitrated product.

> Increase of weight, calculated upon the prepared = 15·7 per cent. fibre
> . Loss of weight, calculated upon the unwashed = 32·5 ,, original fibre (dried)
> Loss of weight, calculated upon the washed = 27·6 ,, original fibre (dried)

The soft, brittle fibrous product was orange-yellow in colour, and contained 9·77 per cent. of nitrogen. The rate of ignition was higher than that of the products described above; and the amount of residue was less, although still very appreciable. Gelatinisation with alcohol-ether was somewhat more complete than in the foregoing cases.

(iv) A control nitration carried out upon a sample of dried cotton-wool resulted in a gain in weight of 69·5 per cent. In general behaviour the product resembled very closely the samples of nitrated Posidonia cellulose (XIII., 2, vi); in texture, however, it was more akin to the specimens of nitrated fibre.

Thus, as regards the yields obtained upon nitration, Posidonia fibre differs markedly from jute, and exhibits a similarity to the woods (54).

2.—Complete Nitration : the Fibre as a Source of Explosives.

From the result of an investigation carried out upon the fibre by Smart (18), the difficulty attendant upon the production of a fibre of low ash content would appear to provide the chief obstacle to its employment as the source of a guncotton comparable in stability to Waltham Abbey guncotton. The fibre was prepared by boiling it with 3 per cent. sulphuric acid for three hours, and after washing and drying in an oven was nitrated for twelve hours in a mixture of three parts by weight of sulphuric acid (sp. gr. 1·84) and one part of fuming nitric acid (sp. gr. 1·5). The prepared fibre gave a 72 per cent. yield of an ash-free product containing 12·3 per cent. of nitrogen. The product gave an Abel heat test of 10½ minutes at 170° F.; and when subjected to the Will test at 135° C., 2·5 grams yielded 6·4 milligrams of nitrogen per four hours, the corresponding value for Waltham Abbey guncotton being 6·0 to 6·5 milligrams. The stability was unimpaired after a lapse of three years.

As regards the yield of nitrated product, the fibre thus compares very unfavorably with cotton-wool, and scarcely less so with the more closely related material jute, which according to Mühlhaeuser (55) yielded 136 per cent. of a product containing up to 12·03 per cent. of nitrogen when nitrated for three hours in a similar mixture. It will be noticed that when submitted to the milder nitration described above (XV., 1), a sample of the fibre prepared in the same way gave a yield of 115·7 per cent.; it appears, therefore, that the stronger nitrating mixture acting for a longer period causes a considerable disintegration and consequent loss of the fibre-substance.

In order to test this point further, another portion of the prepared fibre was immersed for 30 minutes only in the strong nitrating mixture used by Smart. The yield in this case was 108·6 per cent., but the nitrogen-content of the product was only 10·1 per cent. Thus, the shorter nitration, although lessening appreciably the loss of fibre-substance, yielded an incompletely nitrated product.

In further connexion with the question of yields, it has been shown (XIII, 3) that the above method of boiling the fibre with 3 per cent. sulphuric acid, preparatory to nitration, results in the loss of 36 per cent. of the fibre-material, including 42 per cent. of the fibre-cellulose ; consequently, the yield of nitrated product, when calculated upon the weight of the original washed and dried fibre, amounts only to 46 per cent., instead of 72 per cent.

It is therefore apparent that a less destructive preliminary treatment of the fibre would be desirable in any nitrating operations conducted upon the large scale ; and in view of the suggestions which have been made from time to time regarding the possibility of utilising Posidonia fibre as a source of guncotton. some attention has been devoted to this aspect of the nitration process.

In the first place, it has already been indicated that the elimination to the requisite extent of the inorganic matter associated with the fibre is a matter of some difficulty. The sulphuric acid treatment, which appears to be the most efficient of the many methods investigated by Smart, reduced the ash to 0·68 per cent. The majority of the methods involved the objectionable feature of a prolonged or repeated exposure of the fibre to the action of mineral acids or caustic alkali ; while, on the other hand, continued shaking of the fibre, alone and with water, gave a product which still contained 2·8 per cent. of ash.

It has been recorded above (VI.) that a sample of the fibre, after a thorough washing with cold water, yielded 3·1 per cent. of ash ; while a hot-water washing reduced the ash to 2·8 per cent. The difficulty of reducing the ash to the desirable maximum of 0·5 per cent. before nitrating the fibre is thus manifest. However, by washing first with hot water and then with hot 20 per cent. acetic acid, the ash was eventually reduced to 0·2 per cent. with a loss of only 5·4 per cent. of the fibre-material ; and probably it would be possible to devise a still more suitable method of washing. The comparative ineffectiveness of dilute sulphuric acid in reducing the ash may perhaps be ascribed to the high percentage of lime in the inorganic constituents of the fibre (Table J.).

A fibre of low ash-content having been obtained in this manner, its behaviour towards the usual nitrating mixture was next investigated.

When nitrated for sixteen hours with the mixture of concentrated sulphuric acid and fuming nitric acid noted above, two samples of the fibre which had been submitted to the preliminary purification with acetic acid yielded, respectively, 82·9 and 82·0 per cent. of nitrated product. These figures correspond to a mean yield of about 76 per cent., calculated on the original washed and dried fibre, as against 46 per cent. when dilute sulphuric acid was used in preparing the fibre for nitration.

Although the yield of nitrated fibre may be considerably augmented in this way, the product proved to be decidedly inferior to that obtained in the manner adopted by Smart; stability tests yielded unsatisfactory results; and it is significant that the mean percentage of nitrogen was as low as 10·40. It is apparent, therefore, that the preliminary treatment of the fibre with dilute sulphuric acid, besides reducing the ash, eliminated material which exerts a prejudicial effect upon the process of nitration and the character of the nitrated product; this result is doubtlessly connected with the differences exhibited by specimens of cellulose prepared from the fibre before and after the prolonged boiling with dilute sulphuric acid (XIII., 3). In other words, the stability of the guncotton prepared by Smart's method is to be associated with the fall in the furfural value of the raw material.

The results of these investigations indicate that the preparation of a stable guncotton from Posidonia, although possible, would be a decidedly wasteful and expensive process; added to which, the large proportion of fine, short fibre is to be classed as a disadvantage Moreover, in considering the possibilities of the fibre as a source of guncotton, it should not be overlooked that the appreciable divergencies which have been observed between different samples of the fibre might well hinder the attainment of the high degree of constancy of composition which is so essential in a service guncotton. It is also to be anticipated that a guncotton produced from a lignocellulose, yielding as little as 50 per cent. of a " furfuroid "-cellulose (XIII., 3, i), would possess characteristics appreciably different from those of a product derived from so pure a source of " normal " cellulose as cotton-wool. A complete set of comparative tests, carried out upon representative samples of the fibre from different localities, would be necessary in order to secure exact data in connexion with these points ; but in view of the necessity for the adoption of a standard service guncotton throughout the Empire it appears extremely unlikely, from any point of view, that the fibre could ever be utilised as a source of guncotton for military purposes.

It may be noted that crude Posidonia cellulose, although readily capable of nitration, is less homogeneous and considerably more reactive than the " normal " cotton cellulose, and should consequently be less suitable for the manufacture of guncotton (56). The results of the nitration experiments described above (XIII., 2, vi) are in accordance with such anticipations.

The highly nitrated fibre might find a limited application as a component of blasting explosives, and a lower nitrated product would appear to be well adapted to the manufacture of " bulk " or shot-gun powders (57) ; but, apart from such minor possibilities, Posidonia fibre can hardly be regarded as suitable for the large-scale production of explosives.

XVI.—DYEING PROPERTIES OF POSIDONIA FIBRE.

The chemical reactivity of the lignocelluloses is attributed to their lignone components, which behave as unsaturated aldehydes and ketones. Among reactions typical of the lignocelluloses are certain characteristic colour reactions given with phenols and aromatic amines ; such reagents, therefore, act as substantive dyes when brought into contact with the fibre. Thus, it has been shown above (XIV., 1) that Posidonia fibre is dyed a deep golden

yellow with aniline salts, while with p-nitraniline the shade is deepened to an intense orange red. The unusually high absorptive capacity of Posidonia fibre in such cases is illustrated by the quantitative data obtained for the phloroglucinol reaction (XIV., 2).

Not only does the fibre combine with phenols and aromatic amines to give rise to coloured products, but it is also capable of reacting with and absorbing colouring matters of widely divergent types ; many of the ordinary dyes, may, indeed, be applied directly to Posidonia fibre.

The peculiar dyeing properties of the fibre, which have often formed the subject of comment (58), are thus to be ascribed mainly to the high amount and reactivity of the lignone components. In this connexion, it may be remarked that the fibre-substance contains no appreciable amount of nitrogen, and that the dyeing properties are independent of the inorganic constituents of the crude fibre.

The behaviour of Posidonia fibre towards dyes has been investigated by Green and Frank (5), who summarise their results as follows :—

"It exerts the greatest affinity for basic colouring matters, with which it is dyed readily without a mordant, thus behaving similarly to jute. Certain acid dye stuffs, which possess also residual basic properties, such as Patent Blue, Alkali Blues, Wool Blues, Acid Violets, Acid Greens, &c., dye it fairly well, though much less readily than wool. On the other hand, the greater number of the ordinary acid dye stuffs, including those of the azo class, such as Orange G, Sorbine Red, Azo Acid Blue. &c., have no affinity for the fibre. Moreover, the fibre exerts only a small attraction for the salt or "substantive cotton" colouring matters, and this applies also to the "sulphide" dye stuffs. This remarkable divergence in behaviour from that of a pure cellulose fibre, such as cotton, is doubtless due to the lignified character of the fibre and partly to the fact that the cellulose is present in the form of a hydrocellulose or oxycellulose."

In the investigations detailed below the fibre was prepared either by submitting it to a short preliminary boiling with 1 per cent. sodium hydroxide solution, or, preferably, by steeping it for two or three days in 3 per cent. sodium peroxide solution at the ordinary temperture. The depth and uniformity of the colour and the lustre of the dyed fibre were thereby enhanced, while the latter treatment also served to bleach the fibre to a light-cream colour and to soften it (XVIII., 28). The dyed fibre may finally be brightened by soaking it in dilute acetic or tartaric acid solution and allowing it to dry in the air (XVIII., 44 and 45). Excellent effects were obtained in this way.

For purposes of comparison, a specimen of wool was dyed under the same conditions in each case.

The dyeing experiments now described fall into two categories, in accordance with the foregoing discussion :—

1.—Developing Dyeing.

As a consequence of the ready fixation of aromatic amino-compounds upon the fibre, interesting results were obtained by submitting it to the process of "developing dyeing." In cases of this kind the aromatic amine still retains its power of diazotisation, and also of coupling with diazo-solutions, after fixation upon the fibre ; the appended results may serve to illustrate the possibilities which arise in this manner.

(i) By steeping the fibre in a dilute solution of aniline sulphate and then transferring to a bath of diazotised p-nitraniline, it was dyed a deep reddish brown.

Wool was dyed a pale orange under similar conditions.

(ii) When stained in a dilute solution of dimethylaniline hydrochloride and afterwards worked in a bath containing diazotised sulphanilic acid solution, the fibre assumed a very uniform rose-pink colour. This result is of particular interest, seeing that it is practically equivalent to direct dyeing of the fibre with the soluble colour, methyl orange. The dyed fibre responds to acid and alkali in the same manner as methyl orange, and might accordingly be employed as an indicator.

Wool, when treated similarly, was coloured red to orange in patches, the dyeing being very uneven and incomplete.

(iii) After staining in a dilute solution of p-nitraniline hydrochloride, the fibre was immersed in dilute hydrochloric acid and diazotised by admitting sodium nitrite solution in the cold. Upon transferring directly to an alkaline solution of β-naphthol, a very satisfactory bright red shade was produced.

Wool gave a very similar result.

(iv) By reversing the above process, $i.e.$, by steeping the fibre in alkaline β-naphthol solution and coupling with diazotised p-nitraniline, the fibre was dyed a very uniform dark-red.

An appreciably lighter shade was obtained upon wool.

(v) Another specimen of the fibre was soaked in p-nitraniline hydrochloride solution, diazotised, and developed in an alkaline solution of phenol, whereby a deep, dull golden tint was produced.

Wool gave a pale-orange colour, but the result was unsatisfactory.

(vi) By using aniline instead of p-nitraniline, as in (v), the fibre was dyed light brown; the result is interesting as an example of dyeing by the direct use of aniline and phenol.

Wool remained practically undyed when treated in the same way.

(vii) The fibre was stained with aniline hydrochloride solution, diazotized, and transferred to an alkaline solution of β-naphthol. A very satisfactory dull-bronze shade resulted.

With wool the colour was light brown, and the result less successful.

Thus, in all the above instances a satisfactory result was achieved with the fibre, which manifestly possesses a greater affinity than wool for the dyes concerned.

2.—Direct Application of Dyes.

(i) A magenta bath was prepared by adding small quantities of acetic acid and alum to a solution of p-rosaniline hydrochloride in about 250 parts of hot water. The wetted fibre, when entered at 40° and maintained in the boiling solution for fifteen minutes, exhausted a bath containing 1 per cent. of dye, calculated on the weight of the fibre. The level magenta shade produced in this manner was deeper than the shade obtained upon wool under similar conditions.

(ii) A hot bath of Victoria Blue B, of similar strength, containing an addition of sodium bisulphate, was rapidly exhausted by the fibre. The effect was very uneven, probably owing to the great absorptive power of the fibre; the shade varied from light blue to blue-green.

Night Blue gave a very similar result.

In both cases, under similar conditions, a very even and pure blue shade was produced upon wool.

(iii) In order to test the behaviour of the fibre towards acid dyes a bath of Acid Violet 6B was prepared, which contained 3 per cent. of dye, calculated on the weight of the fibre, with an addition of acetic acid and sodium bisulphate. By entering the wetted fibre at about 40° and gradually raising to the boil, the dye was readily and almost completely absorbed with the production of a very even, deep violet shade.

The difference in the case of wool was slight, the shade being somewhat lighter.

It is evident from these results that the fibre possesses a remarkable absorptive capacity for the dyes selected for experiment. The basic dyes, such as Victoria Blue and Night Blue, although absorbed with avidity, cannot in any way be regarded as suitable for use with the fibre. The observations of Green and Frank point further to the unsuitability of the " substantive cotton " and " sulphide " dyes. Probably, dyes of the type of the Acid Violets yield the best results of all ; and in the case recorded above it is notable that the dye gives practically the same shade upon wool as upon Posidonia fibre (cf. XVII., 1). In the remainder of the cases investigated, the fibre was dyed appreciably darker than wool under similar conditions. It may be added that the fastness of the dyed specimens of the fibre to bright sunlight was not particularly satisfactory.

D.—POSIDONIA FIBRE AS A TEXTILE MATERIAL.
XVII.—PRELIMINARY CONSIDERATIONS.
1.—General.

As far back as 1910 Posidonia Fibre had been tested in the manufacture of tweed cloths, and Messrs. Middlemost Bros. and Co., of Huddersfield (England), reported after trials that they considered it suitable for this purpose. Later, its value as a material for mixing with cross-bred wools in the manufacture of cloth, blankets, &c., was demonstrated at Gaunt's Woollen Mills, in Victoria, and in England and France.

In the *Manchester Daily Despatch* of 20th May, 1911, it was stated that " several woollen mills have used it and declared themselves satisfied, and even the most cautious of woollen manufacturers are beginning to interest themselves very keenly in the matter."

The *Yorkshire Evening Post* (Leeds) of the same date reported as follows :—" Two firms—one at Pudsey, and another at Low Wortley—had been experimenting with a curious marine fibre discovered in Spencer's Gulf, South Australia. We now learn that other firms in Huddersfield, Batley, and Leeds have been experimenting, and the results arrived at proclaim that there are great potentialities in the new fibre."

Just prior to the war, German manufacturers became interested in the material, and purchased practically the whole of the supply then available in London ; and in March, 1914, an order was received by the London agents of a Sydney firm for 7,000 to 8,000 tons per annum for Hamburg.

It is thus evident that, had the war not intervened, considerable progress would in all likelihood have been made in the use of Posidonia fibre for textile purposes.

We have before us samples of cloth made at Heckmondwike and Huddersfield, stated to contain a mixture of 50 per cent. of Posidonia fibre and 50 per cent. of wool, which are quite presentable samples of tweed ; and suits of clothes made from similar material were worn by the members of the clerical staff of a London company, and were stated to have been quite satisfactory both in appearance and wear.

The important question of the application of Posidonia fibre in the textile industries has thus received a good deal of attention (59) ; and as the material is greatly different from other commercial fibres, its effective utilisation for textile purposes would undoubtedly demand special methods of treatment. The main results of investigations and trials which have been made in this connexion are summarised in the statements quoted below :—

" When carded, the material furnished an excessive amount of short fibre, and on prolonged treatment the greater part became broken up. The fibre was found to be very difficult to bleach, but in the dyeing experiments it was found to behave very similarly to jute.

The fibre could be spun, either alone or mixed with jute, into a coarse yarn suitable for the manufacture of carpets and similar fabrics. There would, however, be excessive waste in the processes of manufacture and the finished products would be of inferior strength." (60)

" As the fibre is somewhat weak and brittle, a large quantity breaks up into ' shorts ' and ' noils,' so that the final yield of carded material is low, and the value of the fibre for textile purposes is greatly reduced.

Marine fibre batches in well with lower quality wool, or with shoddy, for the manufacture of lower grade materials which would be cheaper than a woollen article.

Allowing 3d. per pound as the landed price of marine fibre, and assuming an exceptionally heavy carding loss of 50 per cent., the price of tops made from marine fibre would run out at about 8d. per pound. A top made from coarse wools would cost about 1s. 6d. per pound; therefore a top made from a mixture of 50 per cent. wool and 50 per cent fibre would cost 1s. 1d. per pound. . . . .

It was also proposed to use it as a substitute for jute in the manufacture of backings for oilcloths, linoleums, carpets, rugs, &c. On account of its short staple, the fibre could not be worked on ordinary jute machinery. But it has been carded into an excellent yarn for this class of manufacture." (61)

On the whole, therefore, the fibre has hitherto shown promise as a raw material for certain coarse and rather weak fabrics ; while, in admixture with wool, it has been found suitable for the manufacture of lower grade cloths.

2.—Physical Properties and Structure of the Filament and of the Ultimate Fibre.

Before entering into any investigation of methods designed to modify the physical properties of the commercial " fibre " so as to render it more suitable for textile purposes, it is of importance to ascertain, firstly, to what extent the properties of the Posidonia filament conform to those of a textile filament ; and, secondly, which, if any, of such properties appear capable of undergoing alteration. The following important properties may be selected for this purpose, viz. :—(i) tensile strength, (ii) elasticity and flexibility, (iii) cohesiveness, (iv) durability, (v) lustre, (vi) dimensions and structure of the filament and of the ultimate fibre.

(i) Tensile Strength.

An inspection of Table G demonstrates the low position of the Posidonia filament as regards tensile strength per unit of cross-sectional area. Of the common textile filaments, Posidonia is superior only to wool in this respect ; although, of course, owing to the greater coarseness of staple (Table C), the

strength of an individual filament may often exceed that of a jute filament. The tensile strength of the Posidonia filament is also impaired by the frequent occurrence of flaws (cf. III., 1).

(ii) Elasticity and Flexibility.

The Posidonia filament, probably as a result of its structural peculiarities, exhibits an exceptionally high extension when submitted to a steady longitudinal strain.

The transverse elasticity (flexibility) is, however, very low (cf. III., 2); and the excessive loss of material in the carding operation (XVII., 1), as well as the difficulty experienced in spinning it into yarn, should be ascribed to this factor rather than to the low tensile strength.

The lack of flexibility is, indeed, one of the chief deficiencies of the crude Posidonia filament, considered as a possible textile "fibre."

(iii) Cohesiveness.

Although possessing a low degree of cohesiveness in comparison with such filaments as those of cotton and wool, it is evident from an examination of Plates VI. and VII. that the surface of the Posidonia filament is not absolutely smooth. In addition to the longitudinal ribbed structure, due to the arrangement of the longitudinal strands (II., 2), the filament exhibits a series of transverse annular ridges, corresponding to protuberances in the exterior ultimate fibres (I., 3). As this irregularity is apparently confined to the exterior surface, it is clear that drastic treatment of the filaments is to be avoided, in order not to remove the outer layer of ultimate fibres.

At the best, however, the cohesiveness of the filament is small, and the preparation from it of yarn presents corresponding difficulties.

An idea of the contour of the filament may be gained from the illustrations of the sections of the fibre bundles, which do not show a circular outline. (Plates III., IV., and V.)

(iv) Durability.

It has been shown that Posidonia is almost unique among vegetable filaments in its resistance to chemical influences (cf. X., XII., and XIV., 7); in this respect it entirely surpasses the somewhat similar material jute, which deteriorates rapidly even when merely damp. It also resists bacterial influences (cf. XVIII., 31). This pronounced resistive power of Posidonia fibre may eventually determine some special application for it. With regard to its utilisation as a material for textile fabrics, it is thus evident that the physical characteristics of the filament would be the most unfavorable factor as far as the durability of such fabrics in the ordinary processes of wear and tear is concerned.

(v) Lustre.

The crude washed fibre is practically devoid of lustre.

(vi) Dimensions and Structure of the Filament and of the Ultimate Fibre.

Posidonia filaments vary considerably in size, ranging from fine silky threads to somewhat coarse stiff bristles, which taper from a fairly thick butt to a fine point. A reference to Tables B and E reveals not only great discrepancies in thickness as between filament and filament, but also equally striking variations between different portions of the same filament. The uniform thickness of staple desirable in a textile filament is thus conspicuously lacking in Posidonia.

Table A illustrates the comparative shortness and irregularity of staple in the case of Posidonia, which is a serious disadvantage in a filament of such coarseness.

The dimensions of the filament thus interpose a formidable obstacle to its use in the manufacture of any but low-grade fabrics.

The investigation of the structure of the Posidonia filament (I. and II.) shows that it consists of a complex aggregate of longitudinally oriented ultimate fibres, averaging possibly 1 mm. in length. These are, indeed, so minute that the average Posidonia filament probably contains over 1,000 per centimetre of run. The physical properties of so complex a structure must evidently differ materially from those of the relatively simple filaments of cotton, flax, &c. ; and an attempt has been made above (III., 2) to correlate various physical properties of the Posidonia filament with its structure.

Further, it appears that the physical characteristics of the ultimate fibres are of primary importance in determining the application of the material from which they are derived. The conspicuous differences which exist between such fibres are obvious from Table D, which is of considerable importance in discussing the possible applications of Posidonia " fibre." Thus, the ultimate fibre of cotton or flax may be over 50 times as long and three times as broad as the ultimate fibre of Posidonia. On the whole, however, the diameter of the ultimate fibre shows comparatively little variation throughout the series illustrated ; whereas the length, although fairly constant for the same material, varies within wide limits as between different types of material.

The length of the ultimate fibre, it seems, may be adopted as a criterion in determining the textile applications of the material concerned. Materials suitable for fine textiles, such as cotton, flax and hemp, are long-fibred ; those suitable only for coarse textiles and rope-making, such as phormium and jute, have fibres of intermediate length ; while the materials whose ultimate fibres fall below about 4 mm. in length have proved to be little adapted for use in the textile industries. If this criterion is accepted, the low position of Posidonia fibre in the above table would denote a correspondingly low value, *per se*, for textile purposes. It is true that the ultimate fibre of Posidonia does not fall far below that of jute in length (Table D, and Plates XV. and XVI.), but the short staple of Posidonia compares very unfavorably with the long staple of jute ; and length of staple, although of less significance than length of ultimate fibre, is an important factor in determining the applications of fibrous materials.

It may now be pointed out that the materials associated with Posidonia in Table D, *i.e.*, those whose ultimate fibres fall between about 0·5 and 3 mm. in length, are typical products utilised in the paper-making industry. Here, as indeed in all the cases summarised in Table D, other characteristics of the ultimate fibre, besides length and diameter, are of importance ; among these may be mentioned thickness of wall and general conformation. The ultimate fibre of Posidonia, besides being decidedly smaller than that of jute, has a thinner wall, but is otherwise very similar to it (Plates XV. and XVI.). The thickness of the fibre-wall and the contour of the cross-section are illustrated in Plate IV. Other characteristics of the ultimate fibre of Posidonia

are given above (I., 3). All such details are particularly relevant in deciding whether the individuality of the fibre fits it for any specific purpose (cf. XIII., 5 and XX.).

It is, then, evident that the structural characteristics of the ultimate fibre of Posidonia relegate it to a class of fibrous materials used largely in the paper-making industry. Of particular interest, therefore, is the fact that a similar conclusion is reached as a result of the chemical examination of the ultimate fibre. This is clear from Table O, which indicates that esparto, straw, and other typical fibres used in the preparation of the lower grades of paper belong, like Posidonia, to the chemical group of furfuroid-celluloses.

(vii) Summary.

Summing up the results of the above preliminary inquiry, it appears that Posidonia " fibre," when considered in the light of a possible textile material, is lacking in most of the main characteristics selected for examination. Only in resistance to chemical and bacterial influences and in the amount of extension under strain does it show a superiority over any of the usual textile " fibres."

Of the characteristics under review, it is conceivable that by appropriate artificial treatment such physical properties as tensile strength, elasticity, flexibility, cohesiveness, and lustre might be improved within limits ; but it is quite obvious that nothing can be done to overcome the underlying and fundamental disadvantages, for textile purposes, of shortness, coarseness, and irregularity of staple ; complex structure of the filament ; and unsuitable dimensions and chemical character of the ultimate fibres. These considerable limitations should be borne in mind in estimating the possibilities of any process designed to increase the value of Posidonia " fibre " as a textile material.

XVIII. — ATTEMPTS TO MODIFY VARIOUS PHYSICAL CHARACTERISTICS OF THE FILAMENT BY ARTIFICIAL TREATMENT.

In some of the many experiments carried out with the above aims in view, the filaments were treated with various reagents which are known to affect cellulose, or lignocellulose, or both. As a rule, the material showed little or no response to cellulose reagents unless it had been submitted to a preliminary treatment involving the structural disintegration of the natural filament into short ultimate fibres. On the other hand, with lignocellulose reagents the original filaments reacted rapidly.

The material was also subjected to a number of more or less empirical processes which have been described, in patent specifications and elsewhere, for modifying the properties of filaments in the desired directions. A selection of typical processes is detailed below, although the list is not exhaustive.

In order to ascertain the efficacy of any particular treatment, the best and most perfect filaments of those treated were subjected to tests identical with those applied to the original filaments (III.). The breaking strains were similarly calculated in kilograms per sq. mm. of cross-section, while the corresponding extensions were expressed as percentages of the original length of filament between the clips ; so that the recorded results are comparative.

It would have been more satisfactory, perhaps, if a more numerous series of filaments had been tested in each case ; but the lack of uniformity in the diameters necessitated many tedious calculations in each group, and it was thought that the numbers taken would furnish sufficient data upon which to judge the effect of any individual treatment, and to suggest directions for further efforts. (Altogether, measurements for over 1,500 filaments are recorded in this Bulletin.)

It must also be emphasised that samples of commercial Posidonia fibre vary considerably, both in length and robustness of filaments. Several reasons might be advanced in order to account for this, but probably the most feasible is that the plants grow more vigorously in some localities than in others. To eliminate possible errors in this direction, the greater proportion of the tabulated tests were carried out on filaments from one consignment, so that the results might be as nearly comparable as practicable.

Again, although great care was taken in an endeavour to select filaments of equal macroscopic value, yet it is recognised that such a material as the Posidonia filament often contains flaws which might easily escape superficial observation (cf. also III., 1).

For purposes of comparison, the following figures for 100 cleaned, untreated filaments are transcribed from Table E :—

Tensile Strength.			Percentage Extension.		
Upper limit	..	25·05	.. Upper limit	..	7·33
Lower limit	..	12·17	.. Lower limit	..	4·1
Mean value	..	20·15	.. Mean value	..	5·29

In each of the appended summaries of the results obtained with sets of filaments which had been exposed to various methods of treatment, the duration of such treatment is first given ; the number of filaments tested in the machine is indicated in the second column of data ; the third column records the limiting values at the thicker end for the diameters of the selected filaments (measured after treatment) ; the fourth column shows the mean breaking strain, expressed in kilograms per sq. mm. of cross-sectional area ; and the fifth column gives the mean percentage elongation under the breaking strain (cf. Tables E and F). The calculations were made as described in III., 1.

1.—Water (hot).

The filaments were boiled for half-an-hour with distilled water, after which they were washed and air-dried (62). Results—

½ hour .. 20 .. 0·173 to 0·073 mm. .. 18·85 .. 6·69

The treated material was cleaner and of better appearance, but otherwise it showed little difference from an ordinary sample of the original " fibre."

Selected filaments were also boiled in distilled water for five minutes, and tested while still moist. Beyond a slight improvement in elasticity, very little alteration was evident. The mean breaking strain of the twenty filaments tested was 18·52, and the percentage extension 7·1. The diameters ranged from 0·146 mm. to 0·093 mm.

2.—Sodium Carbonate Solution (1 per cent., hot).

The filaments were boiled for one hour in a 1 per cent. sodium carbonate solution; they were then washed free from alkali and air-dried (62). Results—

1 hour :. 20 .. 0·16 to 0·086 mm. .. 17·34 .. 5·57

The filaments were brighter, softer, and a little darker; they were also not quite so brittle as originally, although the improvement was not very marked.

3.—Sodium Hydroxide Solution (1 per cent., hot).

In all cases of treatment with caustic soda solutions, the filaments were afterwards washed successively with warm water, dilute acetic acid, and a further quantity of warm water, and were finally air-dried.

The results obtained by boiling the filaments in a 1 per cent. solution of this reagent for various periods are summarised below : —

5 mins.	..	20	..	0·153 to 0·053 mm.	..	17·95	..	4·75
15 mins.	..	30	..	0·193 to 0·073 mm.	..	16·81	..	4·97
1 hour	..	30	..	0·146 to 0·073 mm.	..	15·45	..	7·03
2 hours	..	30	..	0·166 to 0·086 mm.	..	17·20	..	7·48
3 hours	..	30	..	0·153 to 0·066 mm.	..	16·16	..	7·44

These figures suggest that the treatment tends to influence the elasticity favorably. The harshness of the filaments was reduced, and the feel thus improved. In all cases of treatment with alkali, the filaments acquired a slight lustre and also a pronounced yellow colour. In contact with hot alkaline solutions the colour was deepened to a brownish tint.

In order to illustrate the discrepancies which may occur between different samples of commercial Posidonia Fibre, the following comparative results may be quoted for filaments selected from another consignment of the material forwarded to us from the same locality. The reagent was 1 per cent. caustic soda solution, applied in the manner just described :—

5 mins	..	20	..	0·173 to 0·08 mm.	..	21·8	..	5·62
3 hours	..	20	..	0·16 to 0·066 mm.	..	19·65	..	4·75

When compared with the corresponding values in the preceding summary, these data indicate that the second sample was of superior quality to the first. It is also to be noted that no beneficial influence of the reagent upon the elasticity of the filaments is apparent in this instance.

4.—Sodium Hydroxide Solution (5 per cent., cold).

When immersed in a 5 per cent. caustic soda solution, particularly when the treatment was extended to twenty hours, the filament became more supple, and softer to the feel.

1 hour	..	20	..	0·16 to 0·066 mm.	..	16·91	..	5·63
5 hours	..	20	..	0·126 to 0·08 mm.	..	16·95	..	6·17
20 hours	..	20	...	0·133 to 0·08 mm.	..	17·2	..	5·24

5.—Sodium Hydroxide Solution (10 per cent., cold).

The results obtained with a cold 10 per cent. solution of caustic soda were very similar to those recorded above for a 5 per cent. solution.

½ hour	..	20	..	0·12 to 0·04 mm.	..	16·09	..	5·34
1 hour	..	20	..	0·166 to 0·073 mm.	..	21·37	..	3·7
5 hours	..	20	..	0·153 to 0·073 mm.	..	18·37	..	4·25
20 hours	..	20	..	0·126 to 0·066 mm.	..	15·95	..	6·22

6.—Sodium Hydroxide Solution (15 per cent., cold).

With 15 per cent. caustic soda the lustre and feel of the filaments were further improved, and in one series of measurements an exceptionally high percentage elongation was obtained, pointing again to an influence of the reagent upon the elasticity (cf. 3).

10 mins.	..	20	..	0·133 to 0·06 mm.	..	15·12	..	6·54
30 mins.	..	20	..	0·146 to 0·08 mm.	..	16·53	..	6·94
1 hour	..	20	..	0·146 to 0·08 mm.	..	19·60	..	5·43
5 hours	..	20	..	0·146 to 0·08 mm.	..	15·53	..	8·26

7.—Sodium Hydroxide Solution (20 per cent., cold).

10 mins.	..	12	..	0·133 to 0·08 mm.	..	20·09	..	6·59
30 mins.	..	12	..	0·133 to 0·06 mm.	..	16·61	..	5·37
1 hour	..	12	..	0·186 to 0·086 mm.	..	21·20	..	7·29
5 hours	..	12	..	0·146 to 0·086 mm.	..	17·87	..	6·15

8.—Sodium Hydroxide Solution (25 per cent., cold).

10 mins.	..	12	..	0·173 to 0·086 mm.	..	23·32	..	4·24
30 mins.	..	12	..	0·126 to 0·068 mm.	..	22·63	..	5·57
1 hour	..	12	..	0·12 to 0·073 mm.	..	15·94	..	6·25
5 hours	..	12	..	0·113 to 0·086 mm.	..	12·57	..	4·48

9.—Sodium Hydroxide Solution (33 per cent., cold).

1 hour	..	12	..	0·113 to 0·06 mm.	..	15·96	..	3·93

Making due allowance for the considerable variations in the recorded values which must be ascribed to adventitious circumstances, it may be concluded that both tensile strength and elongation suffer when the filament is submitted to prolonged immersion in strong solutions of sodium hydroxide in the cold, although in some cases the weaker solutions appear to exercise a favorable influence upon the elongation. The lustre of the material is improved, but on the whole no particular benefit seems to be derived from the treatment. A similar conclusion may be drawn from the following data for the treatment of the material with hot sodium hydroxide solutions ; in each case the heating was accomplished on the water-bath at constant volume :—

10.—Sodium Hydroxide Solution (15 per cent., hot).

1 hour	..	20	..	0·146 to 0·073 mm.	..	20·02	..	5·71
5 hours	..	20	..	0·126 to 0·066 mm.	..	15·9	..	5·63

11.—Sodium Hydroxide Solution (25 per cent., hot).

1 hour	..	20	..	0·173 to 0·066 mm.	..	14·55	..	6·61
5 hours	..	20	..	0·14 to 0·073 mm.	..	16·71	..	5·92

12.—Schweizer's Reagent (cold).

When soaked in freshly prepared Schweizer's reagent for periods ranging up to twenty hours, the filaments swelled slightly, but were not dissolved to any appreciable extent. The treatment, however, serves to accentuate the external structural features (cf. II., 2), and thus in all likelihood increases the cohesiveness of the filaments (XVII., 2, iii).

After washing with dilute acid, followed by water, the treated material exhibited a faint green tint, and possessed a somewhat improved lustre and softer feel. The flexibility was also noticeably greater, as in some cases it was possible to tie numerous knots in the filament without breaking it; this cannot be done with the crude filament. No advantage in this last respect appeared to be gained by continuing the treatment beyond two minutes.

¼ min.	..	12	..	0·16 to 0·1 mm.	..	22·06	.. 7·47
2 mins.	..	12	..	0·146 to 0·093 mm.	..	20·73	.. 5·49
5 mins.	..	12	..	0·126 to 0·086 mm.	..	15·58	.. 4·93
30 mins.	..	12	..	0·133 to 0·06 mm.	..	16·99	.. 4·97
1 hour	..	12	..	0·173 to 0·08 mm.	..	17·81	.. 4·71
5 hours	..	12	..	0·146 to 0·073 mm.	..	20·05	.. 5·25

A portion of another consignment of crude "fibre" was treated with Schweizer's reagent for corresponding times, the same number of filaments being also tested in each case. The mean tensile strengths were generally a little lower with these specimens; otherwise, in appearance, degree of flexibility, and general characteristics, the treated filaments corresponded with the first series examined.

13.—Zinc Chloride Solution (hot).

When digested with a strong aqueous solution of zinc chloride, between 80° and 100°, the main characteristics of the filament remained substantially unaltered.

14.—Sodium Hydroxide Solution (27·5 per cent., cold), followed by Carbon Disulphide Vapour.

The partially gelatinised filaments obtained by the successive action of 27·5 per cent. sodium hydroxide solution and carbon disulphide vapour (cf. XIV., 7) were aired thoroughly, passed through a bath of 5 per cent. acetic acid, washed with water, and air-dried.

Neither lustre nor feel was improved by this treatment; and both the gelatinised filaments and the final dried ones were rendered noticeably weaker. The treated filaments possessed a drab to yellowish-brown colour; they had been reduced in diameter, and, under the microscope, broken external ultimate fibre-strands were visible.

The diameters of 22 tested filaments ranged from 0·146 to 0·066 mm.; the mean breaking strain was 12·94, and the percentage elongation 5·3.

In another series of tests, the filaments were carried through the above operations, and then steeped for some time in a 40 per cent. formalin bath. After a final washing with dilute acetic acid and water, twelve of the air-dried filaments, ranging in diameter from 0·146 to 0·066 mm., gave a mean breaking strain of 9·89, and an elongation of 7·7 per cent. These values suggest a still more pronounced fraying of the filaments.

In a third test, after the exposure to the action of carbon disulphide vapour, the filaments were aired, steeped in 40 per cent. formalin, and air-dried. The mean values obtained for a series of twelve filaments, exhibiting the same variation in diameter as before, were intermediate in position between the two series recorded above, viz., 11·27 and 7·3.

The treatment is therefore devoid of value.

15.—Carbon Disulphide.

Selected filaments after immersion in carbon disulphide at the ordinary temperature for 24 hours showed an increase in tensile strength and elasticity, but a more prolonged treatment failed to confirm the first result.

24 hours	..	12	..	0·173 to 0·08 mm.	..	23·41	.. 8·92
48 hours	..	12	..	0·193 to 0·093 mm.	..	19·07	.. 5·29

The original values obtained are borne out by the following measurements made upon selected filaments which had been boiled for two hours with 1 per cent. sodium hydroxide before being immersed for 24 hours in the carbon disulphide. The filaments were boiled for five minutes with water and air-dried before being tested.

24 hours	..	12	..	0·146 to 0·086 mm.	..	21·21	.. 7·53

16.—Nitric Acid (fuming, cold).

Fuming nitric acid (sp. gr. 1·5) imparted a dull orange-brown colour to the material. The diameter and tensile strength of the filament were reduced; the elasticity was increased considerably, as evidenced by the readings for the breaking elongation.

2 mins.	..	12	..	0·12 to 0·08 mm.	..	9·49	.. 11·33
5 mins.	..	12	..	0·16 to 0·08 mm.	..	7·44	.. 14·66
10 mins.	..	12	..	0·133 to 0·053 mm.	..	5·94	.. 12·64
20 mins.	..	12	..	0·14 to 0·1 mm.	..	7·95	.. 13·74

17.—Nitric Acid (concentrated, cold).

Concentrated nitric acid (sp. gr. 1·42) affected the filaments in a similar manner, but the results were not quite so pronounced as with the fuming acid. After five hours' treatment most of the filaments had undergone disintegration.

5 mins.	..	12	..	0·12 to 0·073 mm.	..	9·32	.. 6·59
10 mins.	..	12	..	0·12 to 0·066 mm.	..	8·20	.. 8·25
30 mins.	..	12	..	0·133 to 0·066 mm.	..	11·15	.. 11·45
1 hour	..	12	..	0·106 to 0·066 mm.	..	10·26	.. 10·25
5 hours	..	12	..	0·106 to 0·053 mm.	..	5·37	.. 6·56

18.—Nitric Acid (50 per cent., cold).

With 50 per cent. nitric acid the weakening of the filaments was still less marked, as was also the amount of the breaking elongation. The filaments were appreciably softened by this reagent, and the brittleness appeared to have diminished considerably; experiments were therefore continued with more dilute solutions of nitric acid. Prolonged immersion of the filaments in 50 per cent. nitric acid resulted in partial structural disintegration.

½ hour	..	12	..	0·12 to 0·073 mm.	..	14·76	.. 6·6
1 hour	..	12	..	0·10 to 0·06 mm.	..	11·22	.. 5·2
5 hours	..	6	..	0·15 to 0·086 mm.	..	11·23	.. 5·2

19.—Nitric Acid (2 per cent., cold).

After immersion for 24 hours in cold 2 per cent. nitric acid, the material exhibited a light yellowish-brown colour; it was also softer to the touch, and a little more lustrous. Both the elasticity and the flexibility had increased greatly, while the tensile strength, instead of suffering, had also improved somewhat as a result of the treatment. The brittleness had been overcome to such an extent that it was possible to twist the filaments forcibly, and to knot them repeatedly, without breaking them. The appended summary of results will serve to illustrate the marked nature of the change :—

24 hours   ..   10   ..   0·16 to 0·104 mm.   ..   24·84   ..   10·69

20.—Nitric Acid (1 per cent., cold).

Nitric acid of 1 per cent. strength, when applied in a similar manner to filaments which had been kept in boiling water for a few minutes, effected an almost identical alteration in their properties, with the favorable exception that the staining was in this case very slight. There is little advantage to be gained by using the stronger (2 per cent.) acid.

20 hours   ..   20   ..   0·143 to 0·091 mm.   ..   22·09   ..   10·61

A graphic representation of the striking improvement in the extension given by filaments which have been submitted to this treatment is reproduced in Plate XVIII. Of the filaments selected for this purpose, ten were used for control measurements, and ten others were chosen from the remainder after immersion in 1 per cent. nitric acid, in the cold, for twenty hours. The results of the tests made on the crude filaments are represented by continuous lines, while the broken lines represent the ten chemically treated filaments. Not only do the latter filaments commence to stretch under a much smaller strain than the former, but the enhanced extension is sustained throughout the test until the breaking strain is reached.

A comparison of the extensions corresponding in each case to the intermediate strain of 75 grams is instructive. The mean value for the crude filaments is 0·6 per cent.; for the treated filaments it is no less than 4·5 per cent., *i.e.*, the extension of the filament under a definite strain has been increased by chemical treatment to seven and a half times its initial value. This result may be accepted as a numerical expression of the increase of elasticity exhibited by the filaments after the treatment described; and there is an accompanying and apparently commensurate improvement in the flexibility. The method is therefore of exceptional interest.

21.—Hydrochloric Acid (1·5 per cent., cold).

The pronounced success achieved with dilute nitric acid suggested the application of other dilute mineral acids. Dilute hydrochloric acid of the above strength scarcely stained the material, although it improved the lustre slightly, and also exercised a distinctly favorable effect on the elasticity and flexibility. The results, however, were inferior to those obtained with nitric acid—

24 hours   ..   10   ..   0·146 to 0·104 mm.   ..   20·54   ..   8·85

As in the preceding case, the filaments were boiled for a few minutes with water before being immersed in the cold acid. The same preliminary treatment was also adopted in all the succeeding instances of treatment with sulphuric acid.

22.—Sulphuric Acid (1·5 per cent., cold).

When the " fibre " was left in contact for two hours, in the cold, with
·1·5 per cent. sulphuric acid, both the lustre and the feel were improved ;
there was also a very marked increase in elasticity and flexibility. The
colour of the material was not altered appreciably.

2 hours .. 12 .. 0·120 to 0·093 mm. .. 23·09 .. 9·17

Prolonged treatment with acid of the same strength for 24 hours gave
somewhat inferior results : -

24 hours .. 12 .. 0·133 to 0·093 mm. .. 22·17 .. 6·77

23.—Sulphuric Acid (1 per cent., cold).

Treatment with cold 1 per cent. sulphuric acid for one hour gave excellent
results ; at the same time this method is probably the most economical of
those investigated.

1 hour .. 12 .. 0·143 to 0·093 mm. .. 24·86 .. 8·46

24.—Sulphuric Acid (75 per cent., cold).

Samples of the material were immersed for short periods in concentrated
sulphuric acid which had been diluted with half its volume of water (c. 75 per
cent.). The samples were then transferred rapidly to a large volume of water,
washed well with further quantities of water and dilute ammonia, and air-
dried.

. When treated for half-a-minute with acid of this strength, the colour
darkened somewhat, and the harsh feel of the filament remained. Consider-
able weakening occurred, and the elongation increased in amount. Treatment
for one minute produced approximately the same effects, although the
elongation was not so great. By prolonging the action for two minutes, the
filament became dark brown in colour and very harsh to the touch ; the
diameter was also reduced, a microscopic examination showing that some of
the outer layers had been removed. When subjected to five minutes' treat-
ment, the filaments were largely destroyed. It is thus obvious that the
material is adversely affected by sulphuric acid of this strength.

½ min. .. 12 .. 0·113 to 0·066 mm. .. 10·95 .. 7·3
1 min. .. 12 .. 0·113 to 0·086 mm. .. 13·79 .. 4·2
2 mins. .. 12 .. 0·146 to 0·073 mm. .. 10·06 .. 4·2
5 mins. :. 12 .. 0·146 to 0·08 mm. .. 9·95 .. 3·3

Undiluted sulphuric acid (sp. gr. 1·84) rapidly charred and disintegrated
the filament.

25.—Acetic Acid (20 per cent., cold).

It was next of interest to ascertain whether a weak organic acid would
act at all similarly to dilute mineral acids. Accordingly two portions of a
sample of the " fibre," which had been boiled in water for a few minutes,
were steeped in cold 20 per cent. acetic acid for periods of ten minutes and
·24 hours, respectively. In each case, after washing and air-drying, the samples

exhibited an improved feel and lustre. In addition, the following figures indicate that in the second case both the breaking strain and the elongation had increased to a marked extent :—

10 mins.	.. 12	..	0·146 to 0·093 mm.	.. 18·1	.. 7·02
24 hours	.. 10	..	0·155 to 0·104 mm.	.. 24·17	.. 8·64

26.—Acetic Acid (20 per cent., hot).

After a short preliminary boiling in water, the material was immersed in cold 20 per cent. acetic acid, which was then brought to the boil. In general appearance the resulting " fibre " differed in no way from that which had been treated in the cold. From the following measurements it appears that the hot acid had exerted a somewhat detrimental effect on the tensile strength ; this, however, was by no means so marked as in the case of hot dilute mineral acids :—

..	.. 10	..	0·13 to 0·104 mm.	.. 21·69	.. 8·04

27.—Hydrogen Peroxide Solution (3 per cent.).

The filaments were bleached and rendered softer and more lustrous by immersion for two days in 3 per cent. hydrogen peroxide solution ; they possessed considerable elasticity and flexibility after the treatment, and had much of the appearance of hair. They could be repeatedly tied into knots without breaking ; their tensile strength was above the average ; and, in general, the treatment showed great promise in modifying the properties of the material in the desired directions.

48 hours	... 12	..	0·16 to 0·06 mm.	.. 24·27	.. 6·57

28.—Sodium Peroxide Solution (3 per cent.).

When steeped in a 3 per cent. aqueous solution of sodium peroxide for three days, the material was bleached to a light-cream colour. It became softer and more lustrous, but otherwise was impaired rather than benefited by the treatment.

72 hours	.. 20	..	0·133 to 0·08 mm.	.. 14·68	.. 4·64

29.—Ozonised Air.

In view of the favorable influence of hydrogen peroxide solution upon the " fibre " (XVIII., 27), another sample was submitted to the action of the very similar agent—ozone. After immersion in boiling water for three inutes, the original sample was drained and divided into two similar portions. One of these was reserved for control measurements ; the other was kept, while still moist, for a period of one hour in a stream of ozonised air, passed at the rate of 1 litre per minute, and containing approximately 0·004 gram of ozone per litre.

After exposure, the material was lighter in colour, but otherwise little alteration had occurred. No improvement was manifest in elasticity or flexibility, although possibly the tensile strength had improved slightly. The measurements are summarised below :—

Original filaments..	10	..	0·14 to 0·117 mm.	.. 17·79	.. 6·5
Treated filaments..	10	..	0·13 to 0·104 mm.	.. 20·08	.. 6·09

It was also considered of interest to investigate the action of the same reagent upon filaments which had already been improved, by immersion for one hour in 1 per cent. sulphuric acid (XVIII., 23). The measurements obtained for sets of filaments which had been submitted to the single and double treatments respectively are appended :—

Single
treatment   12 .. 0·143 to 0·093 mm. .. 24·86 .. 8·46
Double
treatment   12 .. 0·133 to 0·106 mm. .. 22·80 .. 8·84

It is thus evident that the ozone treatment had no effect.

30.—Collodion (German Patent 129,420).

Selected filaments were first soaked in alcohol and then passed through a collodion solution (German Patent 129,420). The consequent increase in tensile strength and elongation are very apparent when the measurements made on the treated filaments are compared with the corresponding data obtained for a control set of untreated filaments taken from the same bunch of crude material -

Treated
filaments .. 12 .. 0·153 to 0·10 mm. .. 25·15 .. 8·10
Untreated
filaments.. 12 .. 0·116 to 0·086 mm. .. 19·60 .. 6·17

31.—French Patent 434,966 (63).

A sample of the material was exposed to the action of yeast in a fermentation bath containing sugar and glycerol, but no marked effect was observed even after prolonged treatment. The result is of interest in connexion with the reputed rot-resisting properties of Posidonia "fibre" (64). The lustre was enhanced as a result of the treatment, but the material had darkened in colour. The finer filaments were rendered somewhat more flexible, but the coarser ones retained much of their original brittleness. The diameters of the twenty filaments tested lay between 0·133 and 0·066 mm. ; the mean breaking strain was 16·63, and the corresponding mean elongation was 7·19 per cent.

By steeping a number of the "fermented" filaments for three days in a 3 per cent. solution of sodium peroxide, a soft, lustrous golden-yellow product was obtained, which gave measurements very similar to those just quoted. The diameters of the twenty filaments tested lay between 0·133 mm. and 0·053 mm. ; the mean breaking strain was 15·75, and the corresponding mean elongation was 6·98 per cent.

32.—German Patent 197,965.

A sample of the "fibre" was soaked overnight in a formalin-lactic acid bath, after which the material was drained, maintained for five hours at 40° to 50° under reduced pressure, washed with water, and air-dried. The treated filaments retained their harsh feel, and although the flexibility had been increased the tensile strength was lessened by the treatment.

The twelve filaments tested varied in diameter from 0·14 to 0·06 mm. ; the mean breaking strain was 14·49, and the corresponding percentage elongation averaged 7·07.

A formalin-alum bath was also applied with very similar results.

33.—Glycerol (at 150°).

Selected filaments after being heated in a glycerol bath at 150° for 30 minutes gave mean values very near to those of the original material, viz., 20·73 and 6·2.

Other filaments, after this treatment, were washed with water, air-dried, and immersed in 40 per cent. formalin for 24 hours. The values obtained were 16·11 and 5·45, showing that the filaments had deteriorated as a result of the combined treatment.

34.—Linseed Oil (hot).

Selected filaments were heated in linseed oil on the water-bath for one hour, the surplus oil being then removed by means of filter paper. No advantage was observed as a result, the values obtained being 15·65 and 5·84.

When the filaments were heated in linseed oil to a temperature of 130° for 30 minutes they became so brittle that they broke readily when pressed between paper. This action is probably due to the acids in the oil, because when the filaments were heated under similar conditions in a neutral petroleum bath very little alteration was observed in their properties.

35.—Ammonia (concentrated, cold).

The mean breaking strain of a number of filaments which had been kept in concentrated ammonia (sp. gr. 0·880) for 48 hours was 16·14, and the corresponding percentage elongation was 5·02.

36.—Ammonium Sulphide Solution.

Selected filaments were scarcely affected after remaining in ammonium sulphide solution for fifteen hours; after 24 hours the mean breaking strain was 21·11 and the elongation 6·23; and after 90 hours the values were 21·93 and 7·34. The reagent thus appears to improve the elasticity of the filaments.

37.—Sulphurous Acid Solution.

Sulphurous acid solution appears to affect the tensile strength of the filaments unfavorably; after 24 hours' immersion the mean values given by selected filaments were 14·52 and 5·12.

Note.—*In all the subsequent processes described, the filaments were submitted to a preliminary boiling for 30 minutes with 1 per cent. sodium hydroxide solution, for the purpose of rendering them, if possible, more susceptible to the action of the reagents employed.*

The standard values for filaments treated in this preliminary manner were established as follows:—

Mean breaking strain   = 16·95 kilograms per
                                                sq. mm.

Mean percentage elongation   = 5·85 per cent.
under the breaking strain

38.—Phenyl Hydrazine.

The effect of causing the lignone components of the prepared material to react with phenyl hydrazine was investigated, the reaction being carried out in presence of dilute acetic acid at the ordinary temperature. The washed and air-dried product possessed a deep-orange colour and a silky lustre. The mean values obtained for twelve filaments (diameters 0·166 to 0·086 mm.) were 22·6 and 7·01.

39.—Phenol.

The principle illustrated in the preceding method was tested further by treating a specimen of the material with a slightly alkaline solution of phenol at 100°; the result was to darken the material somewhat and to render it softer and more lustrous. The mean values recorded for twelve filaments (diameters 0·12 to 0·073 mm.) were 19·94 and 5·82.

40.—U.S. Patent 1,156,462.

The filaments to be treated were kept for one hour at 100° in an aqueous solution of sodium carbonate (5 per cent.) and glycerol (10 per cent.). Slight darkening occurred, and the lustre and feel were good, but the essential characters were not improved. The mean values given by twelve filaments (diameters 0·133 to 0·073 mm.) were 14·66 and 6·12.

41.—Formalin (40 per cent.).

Filaments which had been soaked in formalin for 24 hours exhibited an improved lustre and a slightly deeper colour. An increase both of tensile strength and elasticity was observed; and the treated filaments were so flexible as to allow of knots being tied in them. On the whole, the results were encouraging with this reagent.

24 hours .. 12 .. 0·153 to 0·08 mm. .. 19·22 .. 9·63

42.—Schweizer's Reagent and Formalin.

Another sample of the material was submitted to the action of Schweizer's reagent for a short time (XVIII., 12), before being treated with formalin as above. The results showed that there was no advantage to be gained by introducing the Schweizer treatment. The mean values obtained for twelve filaments (diameters 0·126 to 0·073 mm.) were 15·31 and 7·84.

43.—Emulsion of Oil in Soap Solution.

The filaments were only very slightly softened when left for two days in an emulsion of oil in soap solution.

44.—Acetic Acid (10 per cent., cold).

When samples of the material were steeped for 30 minutes in 10 per cent. acetic acid, and then removed and allowed to dry in the air without washing, they exhibited a bright silky lustre; the colour remained practically unchanged.

45.—Tartaric Acid (5 per cent., cold).

By using a 5 per cent. solution of tartaric acid in place of 10 per cent. acetic acid, a deep-cream coloured product with a bright silky lustre was obtained. The effect was enhanced by submitting the samples to a preliminary bleaching process (cf. XVIII., 27 and 28).

46.—Special Measurements made upon Knotted Filaments after Chemical Treatment.

In considering possible methods of obtaining more exact data illustrating the improvement in the flexibility of filaments, after treatment in some of the ways just described, it occurred to us to measure the elongation and breaking strain after tying one or more knots in the filament under test. In this manner, the flexibility is made to exert a direct bearing upon the numerical values obtained.

It has already been stated that in several cases the chemically treated filament could be tied into knots repeatedly, with great ease; whereas, it is rarely, even with the exercise of the utmost care, that a knot can be tied in the crude filament so as to withstand the slightest pull. Simple trials of this kind are sufficient to show the great improvement which can be effected in the flexibility of the filament by suitable chemical treatment; but the numerical values given below for various sets of knotted filaments afford a more exact illustration of the point in question.

In the subjoined tables the first column gives the number of knots tied in the filament; the second, the diameter at the thicker end; the third, the actual weight in grams required to break the filament; the fourth, the percentage elongation at the time of fracture; and the fifth, the position of the break. The distance between the clips was 4 cm., as with the other tests.

(i) *Crude Filaments.*

It was only possible in a limited number of instances to tie a complete knot in the crude commercial filament; and when this had been successfully accomplished the slightest pull was invariably sufficient to break the filament at the knot. No measurements can therefore be quoted in this case.

(ii) *Filaments after Treatment with 2 per cent. Nitric Acid for 24 Hours* (XVIII., 19).

2	..	0·117 mm.	..	100	..	5·0	..	Broke at knot
2	..	0·146 mm.	..	107·5	..	8·5	..	,, ,,
2	..	0·117 mm.	..	64	..	12·5	..	Broke elsewhere
2	..	0·133 mm.	..	80	..	8·0	..	Broke at knot
1	..	0·117 mm.	..	70	..	5·0	..	,, ,,
1	..	0·104 mm.	..	70	..	5·5	..	,, ,,

Mean .. 7·42

(iii) *Filaments after Treatment with 1 per cent. Nitric Acid for 20 Hours* (XVIII., 20).

2	..	0·104 mm.	..	60	..	5·5	..	Broke at knot
2	..	0·117 mm.	..	58	..	7·5	..	Broke elsewhere
2	..	0·117 mm.	..	70	..	5·0	..	Broke at knot
2	..	0·117 mm.	..	62·5	..	6·0	..	,, ,,
1	..	0·104 mm.	..	66	..	7·0	..	,, ,,
1	..	0·093 mm.	..	58	..	4·5	..	,, ,,

Mean .. 5·92

(iv) *Filaments after Treatment with* 1·5 *per cent. Hydrochloric Acid for* 24 *Hours* (XVIII., 21).

2	..	0·104 mm.	..	95	..	4·5	..	Broke at knot	
2	..	0·104 mm.	..	90	..	4·5	..	,,	,,
2	..	0·117 mm.	..	92	..	5·0	..	,,	,,
2	..	0·104 mm.	..	67·5	..	6·0	..	,,	,,
1	..	0·133 mm.	..	90	..	5·5	..	,,	,,
1	..	0·130 mm.	..	95	..	9·5	..	Broke elsewhere	

Mean .. 5·83

(v) *Filaments after Treatment with* 1·5 *per cent. Sulphuric Acid for* 2 *Hours* (XVIII., 22).

2	..	0·082 mm.	..	55	..	4·5	..	Broke at knot	
2	..	0·104 mm.	..	70	..	5·5	..	,,	,,
2	..	0·082 mm.	..	52·5	..	5·0	..	,,	,,
1	..	0·140 mm.	..	117·5	..	7·0	..	,,	,,
1	..	0·104 mm.	..	70	..	4·8	..	,,	,,
1	..	0·140 mm.	..	75	..	7·5	..	,,	,,

Mean .. 5·72

(vi) *Filaments after Treatment with* 1·5 *per cent. Sulphuric Acid for* 20 *Hours* (XVIII., 22).

2	..	0·140 mm.	..	67·5	..	5·0	..	Broke at knot	
2	..	0·093 mm.	..	57·5	..	3·5	..	,,	,,
2	..	0·117 mm.	..	60	..	2·5	..	,,	,,
1	..	0·104 mm.	..	70	..	4·5	..	,,	,,
1	..	0·117 mm.	..	70	..	4·5	..	,,	,,
1	..	0·117 mm.	..	90	..	4·5	..	,,	,,

Mean .. 4·08

(vii) *Filaments after Treatment with* 1 *per cent. Sulphuric Acid for one Hour* (XVIII., 23).

1	..	0·093 mm.	..	82·5	..	7·0	..	Broke at knot	
2	..	0·093 mm.	..	65	..	6·5	..	,,	,,
1	..	0·106 mm.	..	92	..	5·5	..	,,	,,
2	..	0·106 mm.	..	74	..	5·5	..	,,	,,
1	..	0·133 mm.	..	112·5	..	7·0	..	,,	,,
2	..	0·120 mm.	..	92·5	..	7·5	..	,,	,,

Mean .. 6·50

(viii) *Filaments after Treatment with cold 20 per cent. Acetic Acid for 24 Hours*
(XVIII., 25).

2	..	0·093	mm.	..	55	..	6·0	..	Broke at knot	
2	..	0·104	mm.	..	75	..	6·0	..	,,	,,
2	..	0·104	mm.	..	80	..	6·0	..	,,	,,
1	..	0·140	mm.	..	92·5	..	7·5	..	,,	,,
1	..	0·117	mm.	..	70	..	4·5	..	,,	,,
1	∴	0·117	mm.	..	100	..	7·0	..	,,	,,

Mean   ..   6·17

(ix) *Filaments after Treatment with hot 20 per cent. Acetic Acid* (XVIII., 26).

2	..	0·093	mm.	..	52·5	..	2·5	..	Broke at knot	
2	..	0·117	mm.	..	80	..	5·5	..	,,	,,
2	..	0·104	mm.	..	72·5	..	5·0	..	,,	,,
1	..	0·117	mm.	..	65	..	4·0	..	,,	,,
1	..	0·093	mm.	..	82·5	..	6·5	..	,,	,,
1	..	0·117	mm.	..	65	..	4·0	..	,,	,,

Mean   ..   4·58

(x) The above tables of data demonstrate the improved flexibility of the chemically treated filaments in a striking manner. That such improvement is general and not selective is brought out by the fact that the 48 filaments enumerated in tables (ii) to (ix) were the only ones selected for the tests. Certainly the most perfect filaments were chosen in each case, but this has been the rule adopted throughout the whole of this investigation. It is thus particularly satisfactory that in no single case was the usual brittleness of the crude filament noticeable after the treatment with dilute acid.

The mean breaking strain has not been calculated in these instances, but from the mean limiting elongations it is possible to obtain some idea regarding the relative merits of the different modes of treatment. Adopting this criterion, the best reagent would be 2 per cent. nitric acid (ii), the second place being taken by 1 per cent. sulphuric acid (vii). Calculating the extensions for a uniform diameter of 0·1 mm., the results are, however, practically identical for both acids.

47.—Summary of Results.

The Posidonia filament consists of numerous thin-walled ultimate fibres without any protective exterior layer (see *e.g.*, Plate IV.), and thus it was found that drastic chemical treatment tends to reduce the diameter and tensile strength, owing to the disintegrating effect exerted upon the composite structure. Hot dilute acids, for example, exert an action of this kind.

With milder chemical agents, however, the disintegrating effect may be avoided ; and, when viewed in the light of the underlying principles discussed above (XVII., 2), the results of the experimental inquiry into the possibilities of improving the filament for textile uses must be considered as highly encouraging.·

Despite the handicap imposed upon such investigations by the unfavorable structural characteristics of the filament, it has been found possible to improve to a marked extent each of the main physical attributes of flexibility, elasticity, and tensile strength. Methods have also been devised for improving the lustre and feel of the material.

It has been pointed out (XVII., 2, ii) that brittleness, *i.e.*, lack of flexibility, provides one of the main obstacles to the use of Marine Fibre as a textile filament; the excessive loss of material in carding, for example, has been ascribed to this factor rather than to low tensile strength. It is, therefore, gratifying to record that by a very simple treatment of the filament with cold dilute mineral acids it acquires a comparatively high degree of flexibility. Dozens of knots may be tied and pulled tight in the treated filaments, while the crude filament usually succumbs at the first test of this kind. The striking improvement in flexibility is also illustrated by the measurements recorded above (XVIII., 46) for the breaking load and elonga-tion of filaments which had been tested after chemical treatment and knotting.

The great increase in flexibility is also accompanied by a corresponding increase in elasticity, *e.g.*, filaments which had been treated with 1 per cent. nitric acid exhibited seven and a half times their original degree of elasticity when submitted to a moderate strain (XVIII., 20).

The improvement in tensile strength was not so pronounced as the increase in flexibility and elasticity: in the most favorable cases it amounted to between 20 and 25 per cent.; and it appears unlikely that the filament is capable of undergoing any appreciable strengthening beyond this point. The mean values obtained for several sets of chemically-treated Posidonia filaments are practically identical with those observed by us for jute filaments (Table G).

In the main these favorable results were achieved by the use of dilute mineral acids, or of 20 per cent. acetic acid, in the cold; and it is of particular interest that in these cases the filaments were improved simultaneously in the three respects mentioned. The collodion process and the treatment with hydrogen peroxide also gave results worthy of note. A summary is appended.

TABLE 8.—IMPROVEMENTS EFFECTED IN THE ELASTICITY, FLEXIBILITY, AND TENSILE STRENGTH OF POSIDONIA FILAMENTS BY MEANS OF CHEMICAL TREATMENT.

Reference No. (Section XVIII.).	Reagent.	Mean Percentage Increase in the Breaking Elongation (Criterion of Elasticity).	Mean Percentage Elongation of Knotted Filaments (Criterion of Elasticity and Flexibility).	Mean Percentage Increase in the Breaking Strain (Criterion of Tensile Strength).
19	HNO_3, 2 per cent., 24 hours	102	7·42	23
20	HNO_3, 1 per cent., 20 hours	101	5·92	10
22	H_2SO_4, 1½ per cent., 2 hours	73	5·72	14·5
21	HCl, 1½ per cent., 24 hours	67	5·83	2
41	Formalin, 40 per cent., 24 hours	65	..	13
25	Acetic acid, 20 per cent., 24 hours	63	6·17	20
23	H_2SO_4, 1 per cent., 1 hour	60	6·50	23
30	Collodion	31	..	28
27	H_2O_2, 3 per cent., 2 days	24	..	20

Most of the above processes also improved the feel and lustre of the " fibre," as was also the case with the Schweizer reagent (XVIII., 12). A bleaching action was noticed with hydrogen peroxide, sodium peroxide, and ozonised air (XVIII., 27, 28, and 29).

From the table it appears that 2 per cent. nitric acid is the best reagent for effecting an all-round improvement in the filament, while 1 per cent. nitric acid or 1 per cent. sulphuric acid may be applied with almost equally good results. Nitric acid of 2 per cent. strength has the disadvantage of staining the material appreciably. It is, of course, quite conceivable that more extensive tests might result in a slight rearrangement of the reagents listed in Table S ; but on the whole it may be assumed that 1 per cent. sulphuric acid, owing to its comparative cheapness, would be the most suitable reagent for large-scale operations. It may be noted, however, that nitric acid or hydrochloric acid yields a cleaner product than sulphuric acid, as the last-named is unable to remove the small nodules of lime which are often attached to the filaments.

Whether the preliminary treatment with boiling water would be necessary in commercial practice is a point which experience would decide, as is also the question of the final washing ; in the laboratory experiments this was accomplished with dilute ammonia. Having outlined the main principles which our experience indicates should be adopted in endeavouring to improve the physical properties of the " fibre " by chemical means, we consider that there is no need to go into further detail in this Bulletin; the determination of the most expeditious and profitable method of applying the results of the laboratory investigations is a matter for large-scale trials.

One point, however, calls for emphasis. The crude commercial filaments are so extremely brittle that they should undoubtedly be treated chemically before being submitted to any drastic mechanical process. Once the untreated filaments are bent under pressure, it is obvious that nothing can be done to remedy the break which will inevitably occur.

The satisfactory results of the treatment with dilute acids lead to the suggestion that the improvement in physical properties is to be connected with the removal of mineral matter from the filament (cf. XV., 2). The inorganic constituents appear to be intimately associated with the organic fibre-material. When the acid liquor from the treated " fibre " is neutralised with sodium hydroxide, a gelatinous precipitate containing both inorganic and organic matter is formed ; and on testing the filtrate from this gelatinous precipitate both lime and magnesia may be detected, the former being present in greater quantity.

Possibly, then, the presence of a protective coating may be assumed, which is easily dissolved in acids but not in alkaline solutions. This assumption would account for the lack of action of strong solutions of sodium hydroxide and similar reagents on the crude " fibre."

It is also probable that these inorganic constituents are largely responsible for the original brittleness of the material ; because after their removal the filaments become flexible and much more elastic.

Possibly the resistance to rot is a further result of the presence of such a coating, which may be either a natural device for the preservation of this portion of the plant or an adventitious result of the prolonged immersion of the filaments in sea-water.

A consideration of the results of tests made on filaments which had been treated with nitric acid of strengths above 1 per cent. indicates that the action of this acid is to some extent specific. It is likely also that the favorable influence of formalin is due partly to the presence of small amounts of formic acid and partly to a specific action exerted by the formaldehyde. The results achieved with certain other reagents, including hydrogen peroxide, present certain anomalous features : and, in general, the nature of the chemical changes which accompany the above alterations in physical properties calls for further investigation. A study of the behaviour of the " improved " material towards alkalies and other reagents which were applied to the crude " fibre " without any pronounced result offers another interesting field for inquiry. A parallel study of jute and other related fibrous materials might also yield results of value. We hope, as opportunity offers, to be able to devote attention to these and other points which for the present must remain unsettled.

E.—NOTE ON A SAMPLE OF WESTERN AUSTRALIAN FIBRE.

As a result of a superficial examination, a sample of Posidonia Fibre forwarded to us from Western Australia (Plate XX.) appeared to possess the same main characteristics as the South Australian material. The specimen had been rolled into tightly packed masses by tidal action, and the rough treatment it had thus undergone was probably the cause of the unusually short staple it exhibited.

It was with difficulty that a sufficient number of unbroken filaments suitable for testing were found. The values observed for breaking strain and extension were in general agreement with those recorded above for the South Australian material : although possibly it may be inferred from them that the filaments from the Western Australian sample were somewhat weaker. The ten filaments tested varied in diameter from 0·14 to 0·104 mm., and gave a mean breaking strain of 16·3 kilograms per sq. mm. of cross-sectional area, and a mean elongation under the breaking strain of 5·29 per cent. (cf. Table E).

It is to be anticipated that the commercial working of such closely knitted bundles of short, broken filaments as those which have come under our notice from Western Australia would present very considerable difficulties ; but the specimen is of interest as affording evidence of the occurrence of the Fibre in quantity—and thus possibly also in workable deposits—in localities well removed from the extensive beds of South Australia.

F.—GENERAL SUMMARY AND CONCLUSIONS.

XIX.—MAIN STRUCTURAL, PHYSICAL, AND CHEMICAL CHARACTERISTICS OF POSIDONIA FIBRE.

The structural, physical, and chemical characteristics of " Marine Fibre " derived from the leaves and stems of the marine submerged flowering plant *Posidonia australis*, Hook. *f.* (*N.O. Naiadace e*), have been submitted to a detailed qualitative and quantitative investigation ; and the material has also undergone a botanical examination and description.

1.—Structural.

Structurally, the Posidonia filament is a complex fibre-aggregate, resol· vable into a congeries of longitudinal strands ; these latter, under appropriate treatment, may be disintegrated further into numerous ultimate fibres, averaging about 1 mm. in length.

The filaments are of comparatively coarse and short staple ; they taper, with occasional swellings, from a thick to a fine end, and also lack uniformity of staple as between filament and filament. The surface is not altogether smooth, but the cohesiveness of the filaments is small. They possess a harsh feel, and are practically lustreless.

2.—Physical.

The tensile strength ·of Posidonia filaments per unit area of cross-section is somewhat less than that of jute ; but owing to the frequent occurrence of flaws in the average Posidonia filament, the disparity in strength between crude Posidonia and jute is found in practice to be considerable.

The Posidonia filament when submitted to a steady longitudinal pull gives an unusually high elongation under the breaking strain, but its lack of flexibility is very pronounced.

3.—Chemical.

(i) Posidonia Lignocellulose.

Chemically, Posidonia " fibre " appears to consist of a reactive lignocellulose intermediate in character between jute and wood lignocelluloses, although it yields a type of cellulose differing from that usually found in association with the lignone complex. The phloroglucinol value is exceptionally high ; and the colour reactions in general are those of a lignocellulose more reactive and less saturated than jute. The proportion of lignone is probably about 40 per cent. Among other noteworthy chemical features of the material are its marked resistance to dilute alkalies and such reagents as zinc chloride solution and the Schweizer reagent ; its susceptibility to the action of the halogens ; and its unusual affinity for dyes.

(ii) Posidonia Cellulose.

Posidonia cellulose is obtained in 55 per cent. yield when the " fibre " is submitted to the chlorine-sulphite process. Among the special chemical characteristics of this type of cellulose is the high furfural value ; this is removed from the values given by the celluloses from jute, woods, and other common lignified tissues, and indicates a resemblance to straw and esparto celluloses. The proportions of α- and γ-cellulose into which Posidonia

cellulose has been resolved, as well as the furfural values of these components, are also in marked agreement with the corresponding data for esparto cellulose. Posidonia cellulose, however, may readily be distinguished from the latter type of cellulose by the fact that it yields no colour with aromatic amines.

A preliminary treatment of the " fibre " with hot dilute sulphuric acid influences very considerably the character of the derived cellulose.

Beyond their technological significance, these results of the study of Posidonia cellulose, when correlated with similar data for other specific compound celluloses, should possess a more general interest in connexion with the task of elucidating the complex chemical and physiological relationships of such products.

XX.—CRITICAL REVIEW OF THE CHIEF INDUSTRIAL ASPECTS OF POSIDONIA FIBRE.

The determination of the structural, physical and chemical characteristics of " Marine Fibre " was mainly undertaken with the object of throwing further light upon its possible industrial applications. The economic importance of determining the most suitable outlets for the " fibre " becomes apparent when it is stated that the workable area of the South Australian deposits alone has been estimated at 240 square miles, corresponding to 4,600,000 tons of the material (65) ; while deposits also occur in other localities (cf. E).

1.—Textile Material.

The most important application to be foreseen is in the textile industry : and for this purpose the low market price of the material is an encouraging factor. It has been estimated, as recently as 1916, that cleaned " Marine Fibre," washed with fresh water, and showing an acid purification loss (XI.) of 5 to 8 per cent., could be landed at a European port at a bare cost of £19 per ton (23).

(i) Fine Textiles.

As demonstrated in the course of this Bulletin, however, the crude " fibre " possesses a number of disadvantageous properties when regarded in the light of a possible textile material—the shortness, coarseness, and irregularity of staple ; the lack of flexibility and cohesiveness ; and, notably, the structural characteristics of the filament are all opposed to its employment in the fabrication of fine textiles.

(ii) Lower-grade Fabrics.

Repeated technological trials appear to have demonstrated that these adverse factors may be overcome to some extent by using " Marine Fibre " as a diluent, in admixture with superior fibrous material, such as wool, in the manufacture of lower-grade fabrics ; the dyeing properties of the " fibre," and its low heat conductivity, may be mentioned as favorable characteristics for such a purpose.

(iii) Coarse Textiles.

Suggestions have also been made for the utilisation of Posidonia " fibre " in the manufacture of coarse textiles, such as guano bags, horse blankets, and woolpacks ; and these might well be realised, in spite of the shortness of staple, and low flexibility and tensile strength. In each of these respects

Posidonia is inferior to jute ; but it is far more resistant than jute to the action of chemical and bacterial agents. Posidonia " fibre " would thus be of especial use in the manufacture of coarse fabrics which might be required to withstand continued exposure to the weather, or to the action of, sea-water or alkaline agents, rather than to offer resistance to friction and strain.

(iv) Improvements effected in the Filament for Textile purposes.

The results of the investigation of Posidonia " fibre " recorded in this Bulletin have an important bearing upon the suggestions which have been put forward for its utilisation as a textile material.

As a preliminary to a brief review of the salient features of this aspect of the work, it should be emphasised that the comparatively low textile value of the crude filament is to be regarded as a consequence of a conjunction of adverse structural and physical characteristics, rather than of isolated factors such as brittleness and low tensile strength. Further, since the physical properties are to a large extent dependent upon the unalterable structure of the filament, it is to be anticipated that such properties will only prove capable of modification within well-defined limits—the possibility of the physical properties of a very short-fibred lignocellulose filament (such as that of Posidonia) being improved to match, or approach, those of longer-fibred compound cellulose or normal cellulose filaments (such as those used in the manufacture of the intermediate and finer grades of textiles) cannot be entertained.

In view of these considerations, it is satisfactory to state that although the fundamental and unalterable structural attributes of the commercial Posidonia filament and of its component ultimate fibres are unfavorable for textile purposes, a marked degree of success has nevertheless been attained in improving various physical properties of the filament (XVIII., 47).

The present investigation goes to show that the main physical defect of the crude commercial filament is its brittleness ; and that possibly lack of tensile strength and elasticity has been unduly stressed in previous publications. It may still be admitted that the tensile strength is low, although in this respect the Posidonia filament is very similar to the much-utilised jute filament ; further, it seems that the structural peculiarities of the Posidonia filament allow only of an increase of about 25 per cent. in the tensile strength as a result of artificial treatment.

The elasticity of the Posidonia filament, under a steady longitudinal strain, is surprisingly high ; and several methods of increasing it to a very striking extent have been devised. In one case, for example, the elasticity of a series of treated filaments was raised to $7\frac{1}{2}$ times the original value (XVIII., 20). The supposed inelasticity of the crude filament is perhaps to be attributed to its extreme brittleness ; a very slight transverse or oblique strain is usually sufficient to occasion fracture. Most of the considerable loss which occurs in carding the " fibre " must be attributed to this lack of flexibility, which is one of the main obstacles to the textile use of the material.

It is thus of particular interest that simple methods of treatment have been discovered (XVIII., 47), whereby a remarkable degree of flexibility may be imparted to the " fibre," enabling the filament to be knotted repeatedly with ease.

The " fibre " may also be rendered softer and more lustrous.

As most of these improvements may be effected simultaneously, and, further, since appropriate methods appear to be capable of application on a commercial scale, the value of " Marine Fibre " for the textile purposes indicated above should increase correspondingly.

2.—Insulating Agent.

The high value of the " fibre " as an insulating agent for heat has been definitely established for some years ; it is stated that in this respect Posidonia is as efficient as hair-felt and superior to such non-conducting materials as asbestos, pumice, mineral wool, &c. (66). As Posidonia " fibre " is now employed extensively for insulating purposes, no further comment is necessary upon this aspect of the question of its utilisation ; but certain points of interest in this connexion have been recorded above (cf. VII. and VIII.).

3.—Minor Possibilities.

Among minor possibilities may be mentioned the suggested use of the " fibre " as a substitute for horsehair and kapok for bedding and upholstery, and as an ingredient, with asbestos, of roofing felts. It has also received notice as a suitable substitute for jute in the manufacture of backings for oilcloths, carpets, rugs, &c. A critical survey of such suggestions is outside the scope of this Bulletin ; but it is probable that any process which would improve the " fibre " for textile purposes would also enhance its value for such applications as those which have just been enumerated.

4.—Source of Explosives.

One other interesting possibility which has attracted attention is that Posidonia " fibre " might form a convenient source of gun-cotton ; but, from the results we have obtained (XV., 2), it appears that with certain relatively unimportant exceptions, the product cannot be regarded as a suitable starting-point for the manufacture of explosives.

5.—Paper-making Material.

The composite lignocellulose structure represented by the Posidonia filament is easily resolvable by chemical means into cellulose units (" ultimate fibres ") averaging, approximately, 1 mm. (1-25th inch) in length. A new series of possible applications is to be associated with these structural units derived from the original filament.

The dimensions of the ultimate fibre of Posidonia (II., 3), as well as its chemical characteristics (XIII., 4), resemble very closely those of the esparto fibre : a strong indication is thus obtained that an outlet for " Marine Fibre " might be sought in the paper-making industry (XIII., 5). The absence of discolouration when Posidonia cellulose is brought into contact with aniline, &c., provides, in one respect, a notable advantage over the widely used esparto cellulose.

In paper-making, as indeed in most of the numerous and rapidly expanding cellulose industries, there is an increasing demand for types of celluloses with specific characteristics for the fulfilment of narrowly defined requirements ; and nothing short of a technological examination, in each case, will be sufficient to determine the most advantageous application of the particular association of properties— structural, physical, and chemical— which centre in the ultimate fibre of *Posidonia australis*.

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6.—Source of Cellulose.

The enormous development of the cellulose technology in recent years—notably the expansion of the viscose (XIII., 2, vii) and cellulose acetate industries, entailing the large-scale production of artificial silk, photographic films, celluloid substitutes, acetate silk, &c.—calls for constantly increasing supplies of the raw material. Hitherto, such supplies have been raised from crop plants and perennial woods, which, in addition to cultivation, demand prolonged treatment before the cellulose can be isolated. In the Posidonia "fibre" Australia possesses a unique and readily-worked source of a cellulose with highly distinctive features : a raw material which is to be envisaged as an enormous potential supply for such industries as utilise cellulose fibres of short length.

With the increasing demand, and particularly in the absence of systematic means of maintaining the supply, the economic position of cellulose appears liable to undergo considerable change during the coming years : but quite apart from such considerations as these, it appears to the authors that a lignocellulose available in millions of tons; directly accessible in the form of separate filaments; independent, therefore, of retting, or more complicated processes; and capable of such ready disintegration into a short-fibred cellulose, must eventually attain an accredited world-position as an economic source of cellulose.

It seems likely that the recognition by technologists of the peculiar conjunction of properties presented by Posidonia lignocellulose, and by the derived Posidonia cellulose, will result in a full exploitation of the potentialities of this remarkable Australian natural product ; and it is with this hope that the results of a laborious but interesting investigation are offered for publication.

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LITERATURE.

1.—Abbreviations.

Allen	..	Allen's "Commercial Organic Analysis."
Ber.	..	Berichte der deutschen chemischen Gesellschaft.
C.E. & M.R.		Chemical Engineering and Mining Review (Melbourne).
Cell.	..	Cross and Bevan's "Cellulose" (1895 and 1918).
C.Y.	..	"The Chemist's Year-book," ed. F. W. Atack (1917).
D.	..	Dingler's polytechnisches Journal.
Dict. App. Chem.		Thorpe's "Dictionary of Applied Chemistry" (1912).
F.A.	..	Bentham's "Flora Australiensis" (1878).
F.T.	..	Hooker's "Flora Tasmanica" (1860).
Imp. Inst. Rep.	..	Selected Reports from the Scientific and Technical Department of the Imperial Institute, No. 58, Part I., Fibres (1909).
J.C.S.	..	Journal of the Chemical Society (Transactions).
J.S.C.I.	..	Journal of the Society of Chemical Industry.
J. Soc. Dyers and Col.		Journal of the Society of Dyers and Colourists.
L.C.	..	"Lectures on Cellulose," C. F. Cross (1912).
Martin	..	Martin's "Industrial Organic Chemistry" (1913).
P. Jahrbuch	..	Pringsheim Jahrbuch.
P.M.	..	Cross and Bevan's "Text-book of Paper-making," 4th ed. (1916).
Rep. Adv. Council	..	Report of the Executive Committee of the Commonwealth Advisory Council of Science and Industry, Melbourne, 2nd July, 1917.
Res. Cell.		Cross and Bevan's "Researches on Cellulose":—Vol 1, 1895–1900; Vol. 2, 1900–1905; Vol. 3, 1905–1910.
S.A Bull. No. 1	..	Bulletin No. 1 of the Department of Chemistry of South Australia: "An Investigation into the Prospects of Establishing a Paper-making Industry in South Australia," by W. A. Hargreaves (Adelaide, 1916).
S.A. Bull. No. 4	..	Bulletin No. 4 of the Department of Chemistry of South Australia: "Marine Fibre," by D. C. Winterbottom (Adelaide, 1917).
S. S. Zeit.	..	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
T.F.	..	J. M. Matthews' "Textile Fibres," 3rd ed. (1913).

2.—References.

THE NUMBER OF THE VOLUME IS IN EACH CASE PRINTED IN HEAVY TYPE.

(1) Rep. Adv. Council, p. 40.
(2) Imp. Inst. Rep., p. 133; S.A. Bull. No. 4, p. 25.
(3) F. T.
(4) F. A.
(5) J. Soc. Dyers and Col., 27 (1911), pp. 169–170.
(6) P. Jahrbuch, 18 (1887), p. 346.
(7) T. F., p. 156.
(8) S.A. Bull. No. 4, p. 25.
(9) C.F., Cross, C.Y., p. 836.
(10) T.F., p. 231.
(11) T.F., p. 391.
(12) T.F., p. 156; C. F. Cross, C.Y., p. 836.
(13) Briggs, J. S. C. I., 37 (1918), p. 44R.
(14) Hitherto unpublished observation.
(15) T.F., pp. 173 and 253.
(16) Private communication.
(17) T. F., p. 253.
(18) Smart, C. E. and M. R., 10 (1918), p. 380; J.C.S.I., 37 (1918), p. 300 T.
(19) S.A. Bull. No. 4, p. 27.
(20) T. F., p. 183.
(21) Cf. Imp. Inst. Rep., p. 134; S.A. Bull. No. 4, pp. 27 and 35.
(22) S.A. Bull. No. 4, p. 22.
(23) S.A. Bull. No. 4, p. 33.
(24) See e.g. Allen, 1 (1910), p. 436; Martin, p. 188; and C.Y., p. 834.
(25) Cf. Imp. Inst. Rep., p. 6.
(26) Cell. (1895), p. 96; Res. Cell., 1, p. 140; Dict. App. Chem., 1, p. 714.
(27) P. M., p. 65.

References—continued.

(28) P. M., p. 142.
(29) C. Y., p. 788.
(30) C. Y., p. 837.
(31) P. M., p. 51.
(32) Cell. (1895), p. 159.
(33) See *e.g.* Cell. (1918), p. 247.
(34) P. M., p. 97.
(35) Cross and Bevan, J. C. S., **113** (1918), p. 184.
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(38) S.A. Bull. No. 4, pp. 28 and 53; see also Imp. Inst. Rep., p. 133.
(39) P. M., p. 52; Res. Cell., **1**, p. 160.
(40) Hargreaves, S.A. Bull. No. 1.
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(45) See *e.g.* T. F., p. 179.
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(47) P. M., p. 63.
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(52) Cell. (1918), p. 104.
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(54) P. M., pp. 61 and 63.
(55) D., **283** (1892), p. 88.
(56) Cf. Cross, L. C., p. 16.
(57) Cf. Nitschnadel, S. S. Zeit., 1912, pp. 257 and 409.
(58) See *e.g.* S.A. Bull. No. 4, pp. 25 and 34; Imp. Inst. Rep., p. 134; Rep. Adv. Council, p. 40.
(59) See also S.A. Bull. No. 4, pp. 25 and 33-36; Imp. Inst. Rep., p. 134; Rep. Adv. Council, p. 40.
(60) Imp. Inst. Rep., p. 134.
(61) S.A. Bull. No. 4, pp. 33-34.
(62) Cf. Hübner and Pope, J. S C. I., **22** (1903), p. 72.
(63) J. S. C. I., **31** (1912), p. 328.
(64) S.A. Bull. No. 4, p. 28.
(65) S.A. Bull. No. 4, p. 10.
(66) Winterbottom, S. A. Bull. No. 4, p. 27; see also Smart and Pecover, "The Commonwealth Engineer" (Melbourne), December 1st., 1917.

PLATE I.— WHOLE PLANT.
Posidonia australis, Hook. *f.* (*N.O. Naiadaceae*).
One-half natural size.

PLATE II PORTION OF A STEM. *Posidonia australis*, Hook *f*. (*N.O Naiadaceae*)
Natural size, showing fibre bundles *in situ*

PLATE III. CROSS-SECTION THROUGH PORTION OF A STEM

Pandanus veitchii, Hook. f. (N.O. Nandineæ)

Showing an area of fibro-bundles scattered in the parenchyma.

(× 65.)

PLATE VI.—SEPARATE FILAMENTS, OR FIBRE BUNDLES
Posidonia australis, Hook. *f*. (*N.O* *Naiadaceæ*).

Showing the swellings on the dorsal surfaces of the outer ultimate
fibres; these appear as dark transverse markings.   The longitudinal
arrangement of the ultimate fibre strands is also evident   × 25
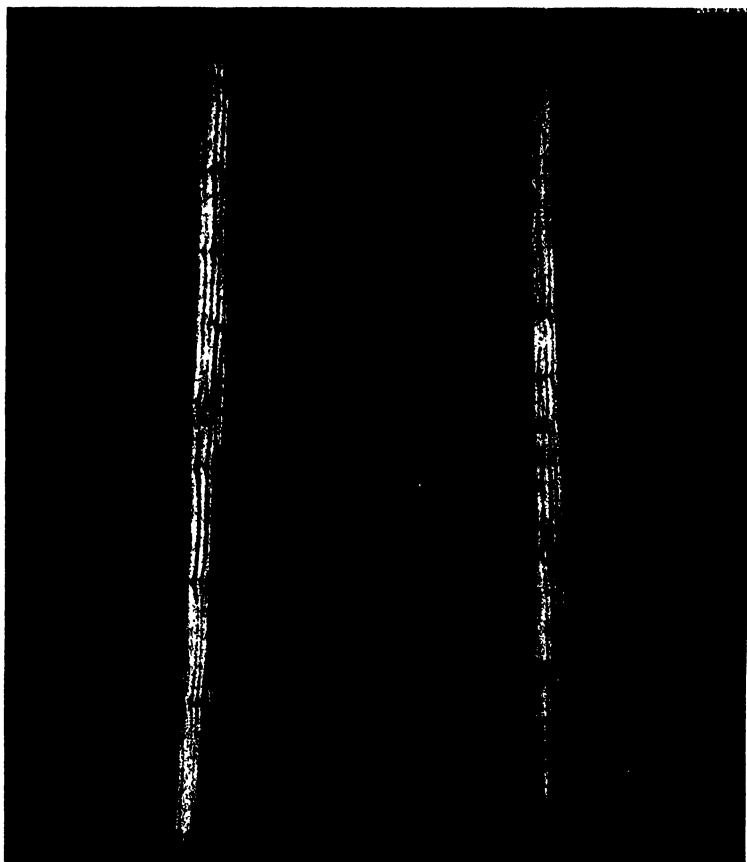
PLATE VII. SEPARATE FILAMENTS, OR FIBRE BUNDLES.

Posidonia australis, Hook. f. (N.O. Naiadaceæ).

Two of the filaments from Plate VI. viewed under a higher power and showing more distinctly the swellings on the dorsal surfaces of the outer ultimate fibres; these appear as dark transverse markings. The longitudinal arrangement of the ultimate fibre strands is also evident × 80.

PLATE VIII.— A PARTIALLY DISINTEGRATED FIBRE BUNDLE

Posidonia australis, Hook. f. (*N.O. Naiadaceæ*)

Showing the dilations on the dorsal surfaces of the outer ultimate fibres; these correspond to the transverse markings in Plates VI and VII. × 100.
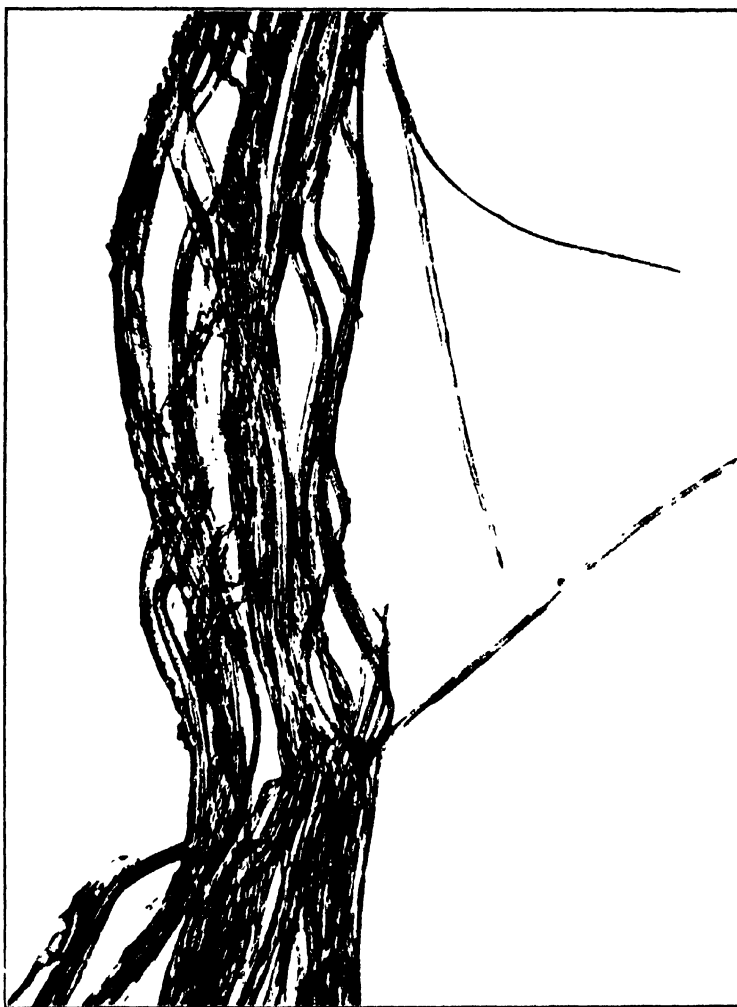
PLATE IX. A SINGLE FIBRE BUNDLE.

Posidonia australis, Hook. f. (*N.O. Naiadaceae*).

Showing the first stage of structural disintegration; separation of the constituent longitudinal strands by the action of bromine vapour   105.

PLATE X.—A SINGLE FIBRE BUNDLE

Posidonia australis, Hook. *f.* (*N.O. Naiadaceæ*)

Separated into its constituent strands This photograph serves to illustrate the resisting properties to bromine vapour of the cementing medium which fastens the ends of the ultimate fibres together. × 105.

PLATE XI. A SINGLE FIBRE BUNDLE

Posidonia australis, Hook. f. (*N.O. Naiadaceae*).

Separated into its constituent strands. The resisting properties to bromine vapour of the cementing medium which fastens the ends of the ultimate fibres together is well shown by the broken end of the fibre bundle.

PLATE XII. A SINGLE FIBRE BUNDLE.

Posidonia australis, Hook. f. (*N.O. Naiadaceæ*).

This photograph illustrates the complete destruction of all cementing material by chlorine water, and the consequent disintegration of the fibre bundles (filament) into minute ultimate fibres. . 105.
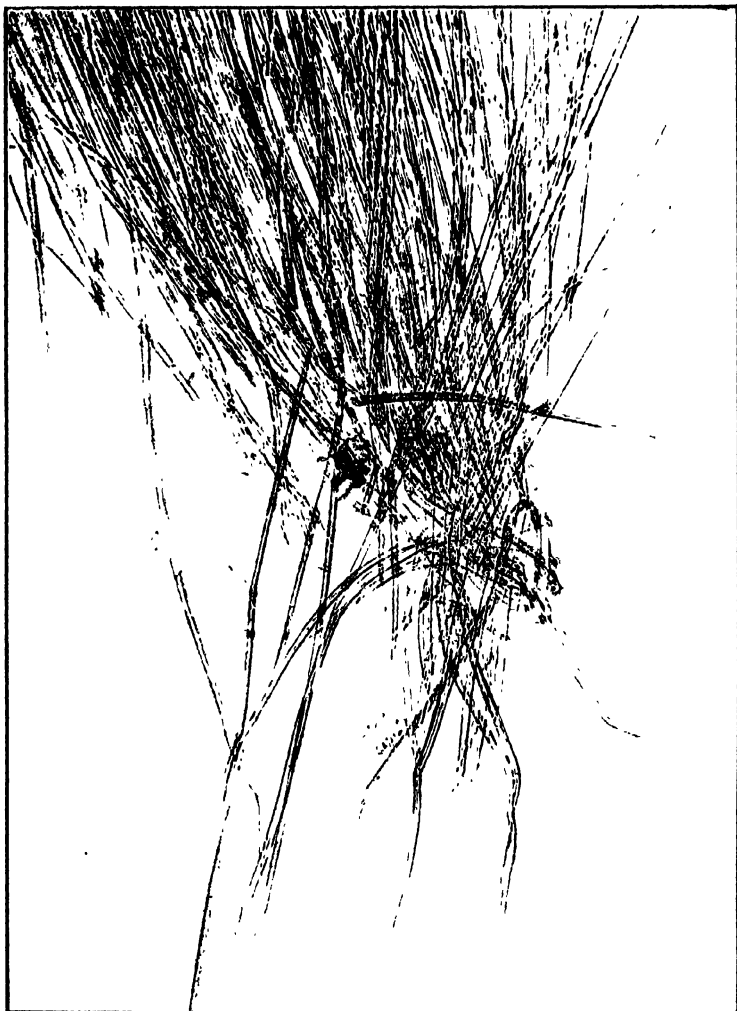
PLATE XIII   A SINGLE FIBRE BUNDLE.

Posidonia australis, Hook. *f.* (*N.O. Naiadaceæ*)

This photograph illustrates the complete destruction of all cementing material by chlorine water, as also shown in Plate XII.   105
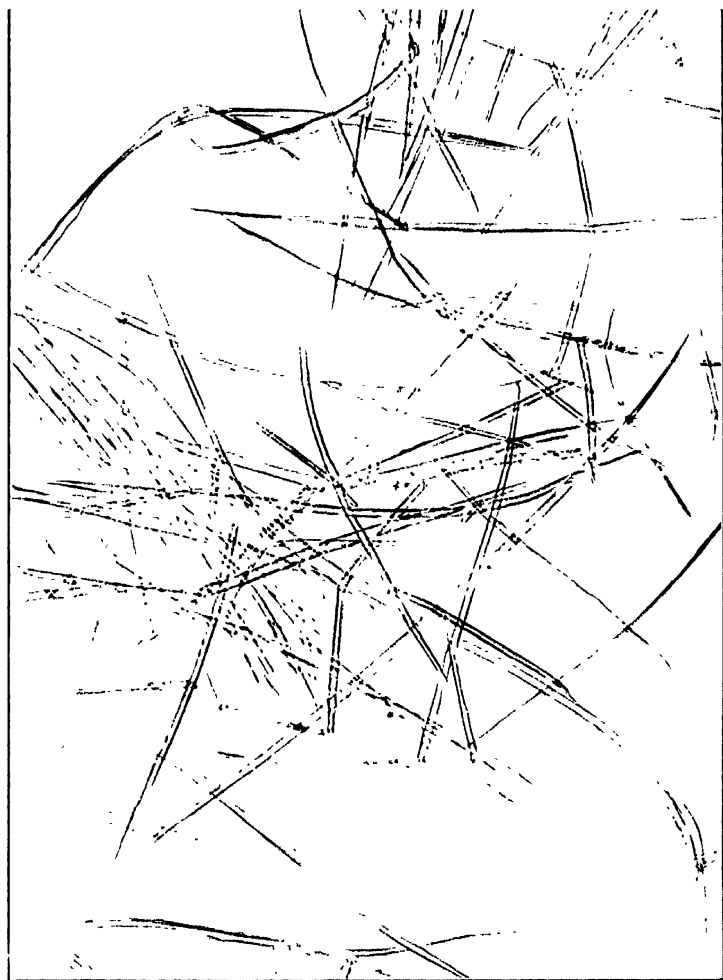
PLATE XIV. —ULTIMATE FIBRES.

Posidonia australis, Hook. *f.* (*N.O. Naiadaceæ*).

Separated by nitric acid and potassium chlorate from the filaments, or fibre bundles. × 105.

PLATE XV.—ULTIMATE FIBRES.

Posidonia australis, Hook. f. (*N.O. Naiadaceæ*).

Separated by sodium hydroxide and chlorine from the filaments. × 105.
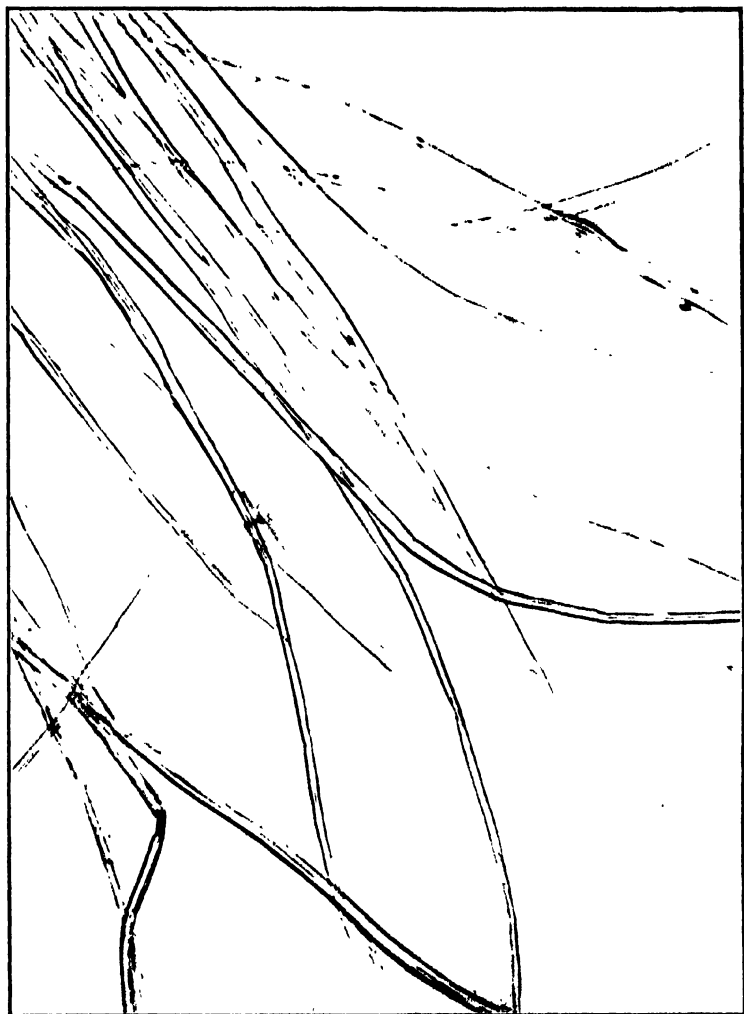
PLATE XVI.—ULTIMATE FIBRES OF JUTE.

These fibres are reproduced for comparison with those of *Posidonia australis.*
(Plates XIV. and XV.).   × 105.
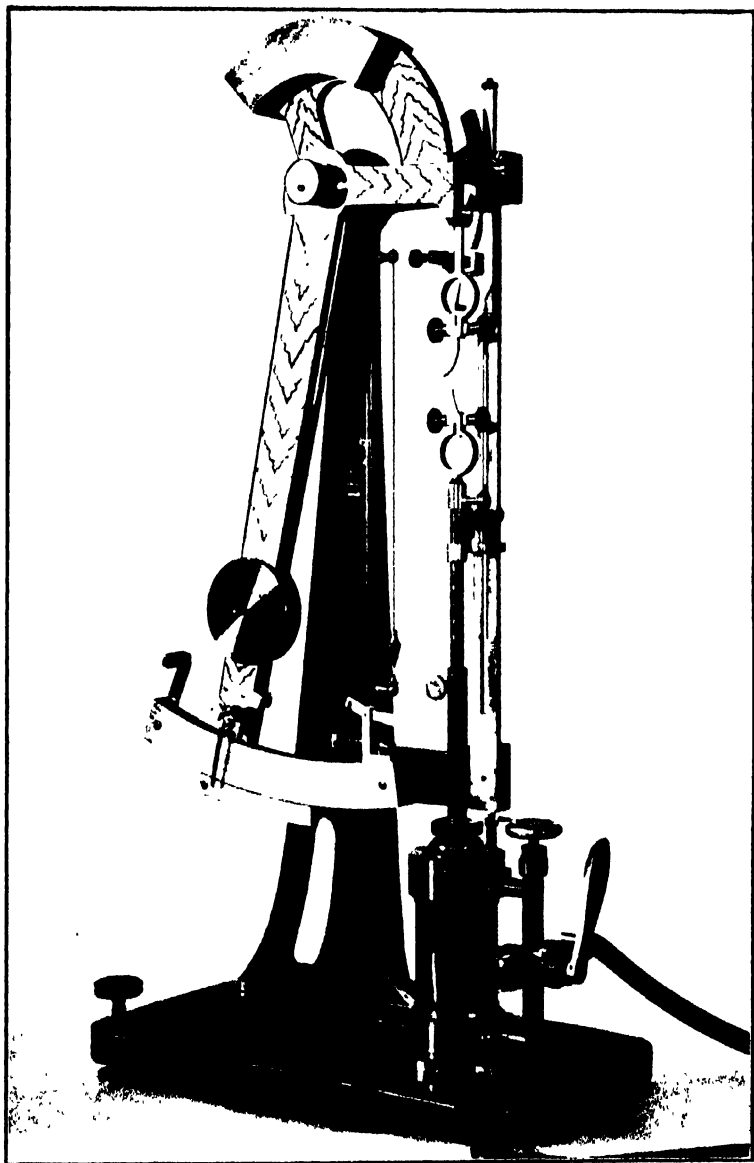
PLATE XVII. -TESTING MACHINE.

Used in the determination of the tensile strength and extension of crude and chemically treated Posidonia filaments. (*See* III., I.)

One-quarter actual size.

Weight in Grams.

Percentage Elongation.
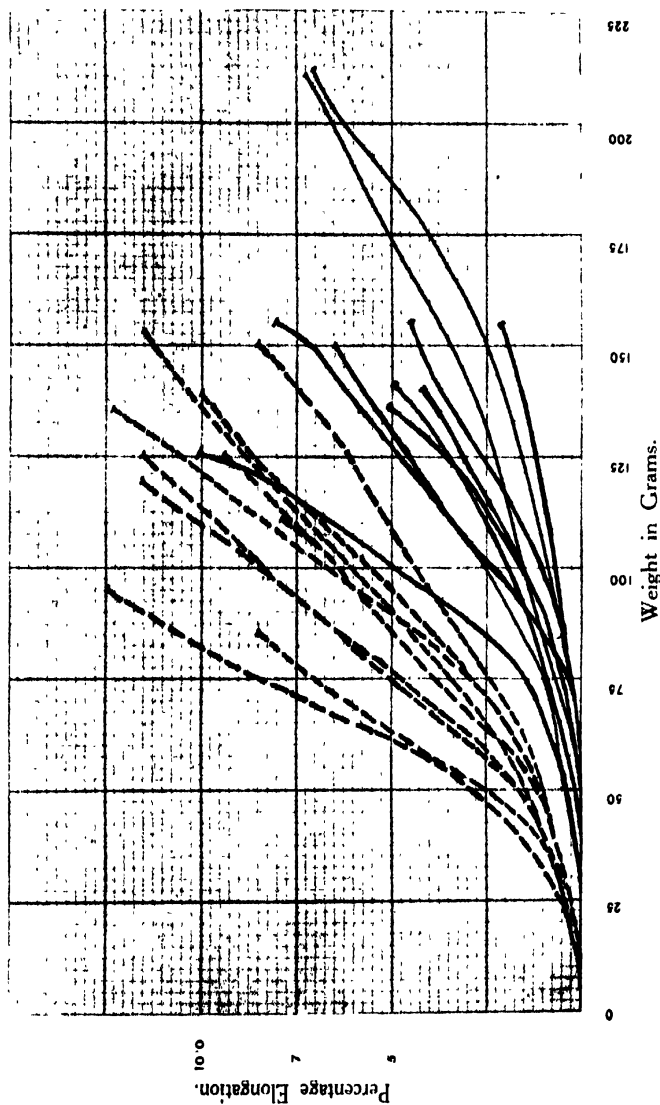
PLATE XVIII.—Extensions given by Posidonia filaments under a gradually increasing strain. The diagram illustrates the gradual extension with increase of load for a series of crude commercial filaments (continuous lines) and for similar filaments which have been treated with 1 per cent. nitric acid for 20 hours in the cold (broken lines). The high extensions of the treated filaments correspond to a marked increase both of elasticity and flexibility. (See III., 2; and XVIII., 21.)

PLATE XIX.—POSIDONIA FIBRE.

As dredged up, washed, and prepared for market at Port Broughton, South Australia.

One-sixth natural size.

PLATE XX.—MASSES OF POSIDONIA FIBRE. As found on the coast of Western Australia. The felted formation is brought about by the action of the waves. (One-third natural size.)

THE PREPARATION OF HALOGENOHYDRINS

BY

JOHN READ

AND

MARGARET MARY WILLIAMS

XLIV.—*The Preparation of Halogenohydrins.*

By John Read and Margaret Mary Williams.

In a previous communication (T., 1917, **111**, 240), we have shown that when ethylene is passed into cold bromine water, two additive reactions occur simultaneously, leading to the production of ethylenebromohydrin and ethylene dibromide respectively. As the first of these reactions takes place with a greater velocity than the second, the method is well adapted to the preparation of ethylenebromohydrin in quantity. Thus, from 200 grams of bromine reacting in a particular experiment, we were able to isolate 85 grams of ethylenebromohydrin and 88 grams of ethylene dibromide, the corresponding relative percentages of ethylene being, therefore, 59 and 41. The bulk of the ethylene thus reacts to form ethylenebromohydrin rather than to produce ethylene dibromide. Owing to the difficulty of effecting a complete isolation of the bromohydrin, the experiments in question are to be regarded as qualitative rather than quantitative, and the latter aspect is reserved for further treatment.

In a further study of the reaction we have now found it possible to improve the yield of bromohydrin by adopting a modification of the original method, to which, incidentally, we have already directed attention (*loc. cit.*, p. 243), that is, by increasing the concentration of the ethylene, and thus accelerating its gross rate of reaction. At the same time, the modified method reduces the concentration of free bromine in the liquid to a minimum throughout the operation.

A current of air is charged with bromine vapour by causing it to pass slowly through a vessel containing an appropriate quantity of the halogen. The gaseous mixture is then passed through a perforated glass bulb into ice-cooled water, which is subjected to vigorous mechanical stirring throughout the course of the experiment. A second perforated bulb, arranged at a distance from the first, admits a regular stream of ethylene into the liquid in the form of numerous minute bubbles. Reaction occurs readily under these conditions, the bromine being admitted at a rate sufficient to maintain at the most a barely perceptible tint in the liquid. The operation may be conducted for a considerable time, and naturally, in practice, the most effective period will be determined by the influence exerted on the reaction by the steadily increasing concentration of ethylenebromohydrin and hydrogen bromide in the solution. This aspect of the reaction is still under consider-

ation, but it may here be noted that in both the original and the modified method the process was continued until the solution had attained a concentration of somewhat more than 14 per cent. of ethylenebromohydrin, determined by direct isolation, the mean value corresponding approximately with a 1·33N-solution of this substance.

The following results of a typical experiment may be quoted, the products having been separated in the manner already described (*loc. cit.*, p. 242) : using 500 c.c. of water, the amounts of ethylenebromohydrin and ethylene dibromide obtained were 82 grams and 54 grams respectively, and the amount of hydrogen bromide present in the liquid at the end was 69·7 grams, estimated by titration. The relative percentage amounts of ethylene corresponding with the above weights of ethylenebromohydrin and ethylene dibromide are 70 and 30 respectively. It is apparent, therefore, that the modified process is superior to the original method in yielding an appreciably higher bromohydrin/dibromide value, the molecular ratio being 1·45 in the original method and 2·3 in the modified process.

As already indicated, the results derived in this manner, although useful for purposes of comparison, are not to be accepted as exact quantitative values, and possibly a more accurate idea of the numerical relationships may be derived from a consideration of the distribution of the bromine in the above experiment. Of the total bromine accounted for (167·3 grams), 62·7 per cent. was utilised in the production of the isolated bromohydrin and 27·5 per cent. was converted to dibromide, whilst the residual 9·8 per cent. represents an apparent excess of hydrogen bromide, the occurrence of which may possibly be due in some measure to decomposition of hypobromous acid into hydrogen bromide and oxygen. Under the conditions now described, however, it seems unlikely that any very appreciable loss of halogen would accrue from this cause; the apparent excess of hydrogen bromide appears rather to be a consequence of the incomplete extraction of the soluble bromohydrin. Accepting this view, that is, adopting the amount of hydrogen bromide formed as a criterion of the yield of bromohydrin, the distribution of the ethylene in the experiment described above would be 75 : 25, corresponding with a molecular ratio of 3·0 as between ethylenebromohydrin and ethylene dibromide.

Further discussion of these values may conveniently be deferred until further data have been accumulated, but the results prove that cold bromine water provides a valuable source of potential hypobromous acid, and that its application in the manner described opens up a very practical and expeditious method of preparing

bromohydrins. That this additive reaction is capable of wide application is indicated by the results of further investigations, which, however, for the most part have not yet been completed. In the case of cinnamic acid, for example, we have been able to show that a similar reaction occurs with great ease, the ratio of the respective amounts of cinnamic acid converted to bromohydrin and dibromide in a particular experiment being about $5\cdot0$ (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 561). Owing to the comparatively high molecular weights of the substances concerned, and also to the ease with which the products may be isolated, the final concentration of bromohydrin in the solution was kept in this case quite conveniently below $0\cdot2N$; the high value of the bromohydrin-dibromide ratio is doubtlessly due partly to this factor.

From the results we have recorded in the case of bromine water, it is evident that chlorine water may similarly be regarded as a highly convenient source of potential hypochlorous acid for use in the preparation of the corresponding chlorohydrins. Bromine rather than chlorine was selected for the initial investigation, owing to the reported comparative facility of combination of hypobromous acid with ethylene (*Annalen*, 1866, **144**, 40; *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 900), and to the greater convenience of manipulation. Our anticipation that chlorine water and ethylene would react similarly was confirmed by a series of preliminary experiments, but, owing to the pressure of other work, the matter had to be left in abeyance for the time being. The continuation of this line of our investigation has now been rendered unnecessary, owing to the recent publication by Gomberg (*J. Amer. Chem. Soc.*, 1919, **41**, 1414) of the results of a detailed examination of this reaction, the principle adopted being that laid down in our original paper, whilst the amounts of ethylenechlorohydrin produced were estimated by means of a refractometric method which appears to meet adequately the requirements of this particular case. From the results given, it would seem that under comparable conditions the reaction in the case of ethylene proceeds somewhat more readily with chlorine water than with bromine water, interpolation revealing that in the preparation of a $1\cdot33N$-solution of ethylenechlorohydrin, the relative percentage amounts of ethylene converted to chlorohydrin and dichloride would be 84 and 11 respectively.

It may be added that a study of the action of chlorine water on cinnamic acid has also given satisfactory results. The details of this last reaction, as well as the results of an extended series of related investigations, are reserved for future publication, but we may remark in this place that sufficient data have been secured to

indicate that both chlorine water and bromine water are capable of wide application in the novel and effective method of preparing halogenohydrins which we have described.

DEPARTMENT OF ORGANIC CHEMISTRY,
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ORGANO-METALLIC DERIVATIVES OF CHROMIUM, TUNGSTEN, AND IRON.

NOTE ON ORGANO-METALLIC DERIVATIVES OF CHROMIUM, TUNGSTEN AND IRON.

By George Macdonald Bennett, m.a., m.sc, and
Eustace Ebenezer Turner, b.a., m.sc.

(Communicated by Prof. J. Read).

It has been shown[1] that anhydrous chromic chloride reacts with aryl-magnesium halides to give compounds which, on decomposing with mineral acids, are quantitatively converted into the respective di-aryl hydrocarbons. The nature of the intermediate compounds, usually (as in the case of the product from phenyl magnesium bromide) orange-red in colour, has not yet been determined, owing to the difficulty of isolating pure substances from the reaction-mixtures, but in view of some experiments (carried out in 1914) on the interaction of phenyl magnesium bromide and anhydrous ferric chloride, the view is now expressed that in thé case, both of chromic and ferric chlorides, organo-metallic derivatives are formed, these being decomposed n presence of mineral acid, so that in the preliminary experiments their formation escaped observation.

Of the two series of organo-metallic compounds, the iron compounds are apparently the more stable. The chromium intermediate compound (phenyl) on treatment with mineral acid, is at once converted into diphenyl, whereas the iron compound is partly so decomposed, the major portion remaining in the ethereal solution. Thus in one experiment, a Grignard reagent prepared from 37·5 grams of bromo-benzene, 4·6 grams of magnesium and 50 ccs. of ether was

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[1] Trans, Chem. Soc., 1914, 105, 1057,

divided into two equal portions. The first was at once decomposed with water and acid and gave 0·6 grams of diphenyl. The second was treated with 5 grams of ferric chloride and gave 4 grams of diphenyl, so that evidently the majority of the initially-formed iron organo-compound remained in the ethereal solution as such.

An attempt was made to isolate an iron organo-compound: the reaction mixture from phenyl magnesium bromide and ferric chloride in ether was treated with water and dilute sulphuric acid and the ethereal solution separated, dried, filtered and evaporated. The dark coloured solid residue so obtained was freed from diphenyl by extraction with light petroleum, when an ochre-coloured solid was obtained. This was washed with water, dried, dissolved in benzene and precipitated by the addition of light petroleum. A greenish solid resulted, which contained iron, was soluble in benzene and depressed the melting point of diphenyl.

Oddo, who has investigated the subject from a different point of view[1] apparently failed to isolate a solid phenylated iron compound, although his conclusions are in substantial agreement with those now put forward.

In the interaction of tungsten chlorides with Grignard reagents, organo-metallic compounds seem to be produced as unstable intermediate products, all attempts to isolate them, however, having at present met with no success.
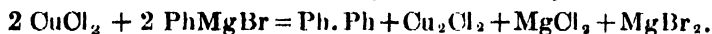
THE ACTION OF CUPRIC CHLORIDE ON ORGANO-METALLIC DERIVATIVES OF MAGNESIUM.

By EUSTACE EBENEZER TURNER, B.A., M.Sc., A.I.C.

IT has been shown[1] that an ethereal solution of phenyl magnesium bromide reacts with anhydrous cupric chloride to give an almost theoretical yield of diphenyl:

$$2\ CuCl_2 + 2\ PhMgBr = Ph.Ph + Cu_2Cl_2 + MgCl_2 + MgBr_2.$$

This method of preparing diphenyl is preferable to that described previously[2] using chromic chloride, since the anhydrous cupric chloride may readily be made by dehydrating the commercial dihydrate. Moreover, in the case of o-tolylmagnesium bromide and iodide, chromic chloride gave a very poor yield of 1 : 1'-ditolyl, whereas it has now been found that anhydrous cupric chloride reacts with o-tolylmagnesium bromide to give the ditolyl in good yield. That the preparation of this hydrocarbon has presented some difficulty in other hands may be judged from the fact that Kenner and Turner[3] rejected the Fittig method in favour of that due to Ullmann.[4]

Attempts to couple two dissimilar groups by means of the cupric chloride reaction have met with no success, as was the case with chromic chloride. Since there is no obvious reason to expect a better yield of (say) toluene in the Fittig reaction:

$$Ph. I + 2\ Na + Me. I = 2\ Na I + Ph.Me,$$

[1] Trans. Chem. Soc., 1919, 115, 559.

[2] Trans. Chem. Soc., 1914, 105, 1057; this Journal. 1919, LIII, 100.

[3] Trans. Chem. Soc , 1911, 99, 2108.

[4] Annalen d. Chemie, 1904, 332. 28.

than in the still hypothetical reaction :

$$PhMgI + MeMgI + 2\,CuCl_2 = Ph.Me + Cu_2Cl_2 + MgI^2 + MgCl_2,$$

both being apparently quadrimolecular reactions, it is probable that the Fittig reaction is of a far more complex nature than is generally supposed. It is not commonly realised, moreover, that the Fittig reaction is by no means capable of universal application, and that actually it is useless in practice for the preparation of several of the more common diaryl-hydrocarbons in any quantity; in these cases either the chromic or cupric chloride method gives good yields, and (which is equally important) very pure products.

It would be expected that cupric chloride would react with the magnesium derivatives of halogen fatty acids to give succinic acids. Although, owing to lack of material, it has not been possible to investigate this matter fully, it is concluded that little success is likely to result from a more exhaustive examination. Thus in some preliminary experiments neither bromoacetic ester nor β-iodopropionic ester reacted in ethereal solution to give the expected succinic or adipic esters. With the simpler ester, a vigorous reaction was observed, but this was probably due to interaction between carbethoxymethyl magnesium bromide and unchanged bromoacetic ester. The iodopropionic ester, on the other hand, was recovered, for the most part, unchanged, à result which can be attributed, no doubt, to the slight reactivity of a halogen situated in the β-position with respect to a carbethoxy-group.

α-Bromobutyric ester, on the other hand, gave an appreciable quantity of s-diethylsuccinic diethyl ester when allowed to react in ethereal solution with magnesium and cupric chloride.

Experimental

Preparation of 1 : 1[1] Ditolyl.

Anhydrous cupric chloride (60 grams) was added to a Grignard reagent made from 51·3 grams of o-bromotolueen,

7·3 grams of magnesium and 200 ccs. of ether. A vigorous reaction set in and was finally carried to completion by heating on the water bath. The orange-red solid (possibly an organometallic derivative of copper) was decomposed with water and dilute acid, the organic portion extracted with ether, and the extract dried, filtered and evaporated. The residue was distilled under diminished pressure and gave a yield of 1 : 1 -ditolyl corresponding to 30 per cent. of the theoretical. The hydrocarbon was very pure and melted at 18˙.

Attempt to prepare α-Benzylnaphthalene.

Benzyl bromide and magnesium react in presence of ether to give not only benzyl magnesium bromide but also considerable quantities of s-diphenylethane, the formation of the latter being decreased if a large excess of magnesium is present. The mixed Grignard reagents were therefore prepared by allowing 31·2 grams of benzyl bromide to react with 9·73 grams of magnesium in presence of 200 ccs. of ether, 41·4 grams of α-bromonaphthalene being added when the whole of the benzyl bromide had reacted. To the solution finally obtained were added 60 grams of cupric chloride. A brisk reaction set in, was carried to completion by heating, and the product worked up as described above. Distillation under diminished pressure gave traces of toluene and naphthalene, but chiefly s-diphenylethane and α : α'-dinaphthyl. No α-benzylnapthalene could be detected.

Formation of s-Diethylsuccinic diethyl ester.

α-Bromobutyric ester (19·5 grams) was added to 2·43 grams of magnesium and 200 ccs. of ether. As soon as a vigorous reaction had set in, 20 grams of cupric chloride were added. Steady reaction proceeded for about half an hour and allowed to become complete at water bath temperatures. The resulting mixture, on decomposing in the usual manner, gave 3·5 grams of s-diethylsuccinic diethyl ester.

PRELIMINARY ACCOUNT OF A MAGNETIC
EXTENSOMETER.

By J. P. V. MADSEN, D.Sc., B.E.

PRELIMINARY ACCOUNT OF A MAGNETIC EXTENSOMETER.

By J. P. V. Madsen, D.Sc., B.E.

INTRODUCTION.

The work described in this paper was carried out in the Electrical Engineering Laboratory of the P. N. Russell School of Engineering at the University of Sydney by several senior students and graduates, under the direction of the author.

As the work has been seriously interrupted in recent years, it is thought that a preliminary account of the investigation and of the results so far obtained may be justified at the present time, pending the completion of the work.

One application of magnetic effects to the measurement of small distances is to be found in the Denny-Johnson Torsion-meter.

In this apparatus the movement between two points on a steel shaft subjected to torsion causes a corresponding displace-

PRIMARY

SECONDARY   SECONDARY

POLE   POLE

ARMATURE
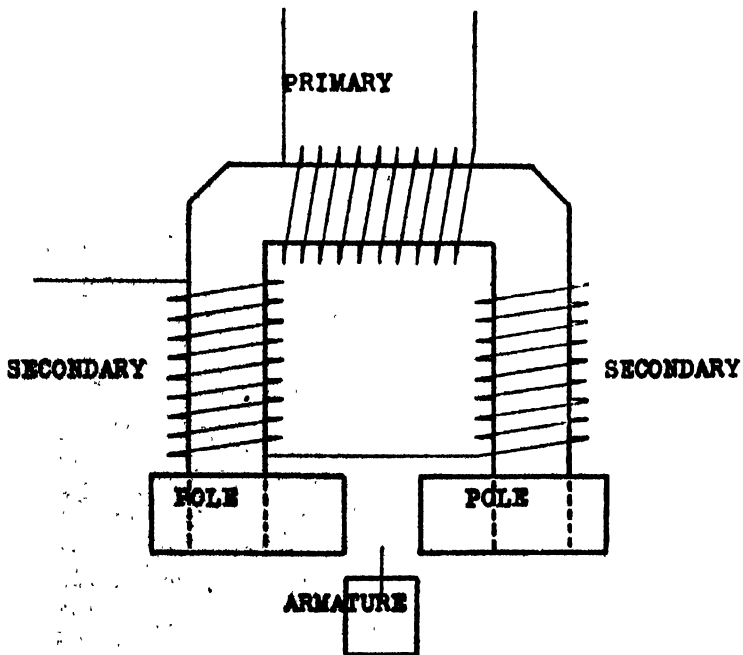
FIGURE

ment between two iron cores relatively to each other. A primary coil is wound over the one core, and is excited by an alternating current. A secondary coil is wound on the second core and the induced voltage is measured by a suitable form of voltmeter. In the apparatus described by Denny-Johnson the greatest movement measured was .2 inches, with the pole pieces set so as to approach one another not closer than .05 inches. Under ordinary circumstances the torsion is measured in about five feet of shafting. The arrangement, though simple, seems unnecessarily bulky, and appeared capable of considerable refinement. With this object, our first efforts were directed towards the improvement of the extensometer portion of the apparatus.

Preliminary experiments were carried out by Messrs. O. le M. Knight and D. P. Herbert, using an arrangement as shown on Fig. 1, in which primary and secondary coils were wound upon a laminated core. In this core a gap was cut to allow the reluctance of the circuit to be controlled by the movement of pieces of iron in the gap.

Experiments were also tried varying the size of the gap. The results showed that with suitable adjustment of gap and plunger, the voltage from the secondary coil could be increased from 250 volts to 300 volts for a movement of the plunger of 1/32 in. This represents a sensitiveness of approximately .4 volts for $\frac{1}{10,000}$ in., and would mean the reduction from five feet to one foot in the necessary length of shaft for the torsion-meter.

The chief objections arose from the presence initially of a considerable magnetic flux which produced a voltage large compared with the amount to be measured, and also gave rise to unnecessarily large initial pull on the plunger.

Experiments were designed to further increase the sensitiveness, and to remove, if possible, the objections referrd to, and were carried out by Messrs. A. Burn, R. A. Holloway, H. G. Fry, and W. E. Pike.

DESCRIPTION OF APPARATUS.

Figures 2 and 3 show the design of the new apparatus. The instrument consists of a core made from stampings of 26-gauge soft iron, with 1/16 in. cover plates. The stampings are riveted together, and milled out to the shape and dimensions shown in Fig. 2.

The legs of the core are wound with primary coils, each coil consisting of about 100 turns of No. 22 S.W.G. cotton-

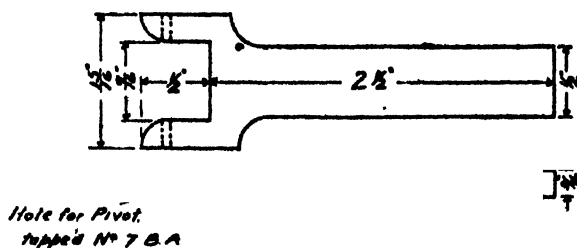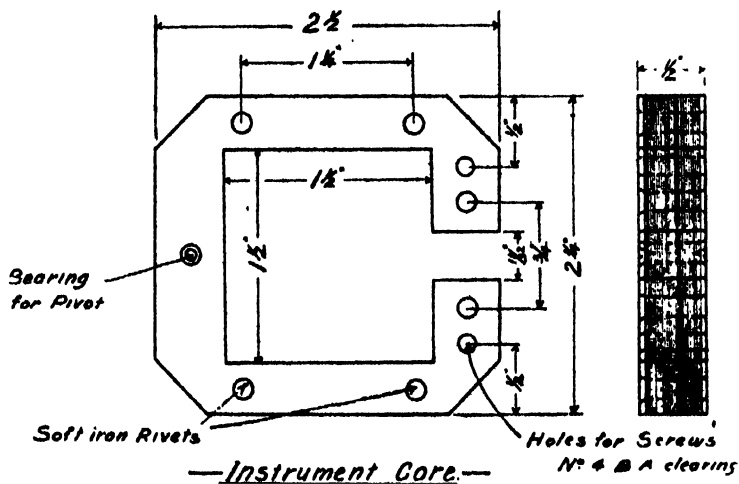# A MAGNETIC EXTENSOMETER.

DETAIL OF CORE AND ARMATURE.

Bearing for Pivot

Soft iron Rivets

Holes for Screws
Nº 4 B A clearing

— *Instrument Core.* —

Hole for Pivot
tapped Nº 7 B A

— *Armature.* —

FIG. 2.

covered wire. The total resistance of the primary coils was
.63 ohms. In the air-gap works a pivoted armature, overwound
with, 676 turns of No. 32 S.W.G. double silk-covered wire.
Total resistance, 10.14 ohms.

When the armature is symmetrically situated with respect
to the air gap, the flux passing through the secondary coil is
zero. A movement of the armature towards either leg of the
core diminishes the air gap on this side and increases it equally
on the other. Accordingly such movement causes flux to pass
in the armature, and hence produces an E.M.F. in the secondary
coil which varies with the distance the armature moves from the
position of symmetry.

CORE

PRIMARY   SECONDARY   PRIMARY

RECTIFIER
COMMUTATOR   RESISTANCE

AMMETER   GALVANOMETER

ADJUSTABLE
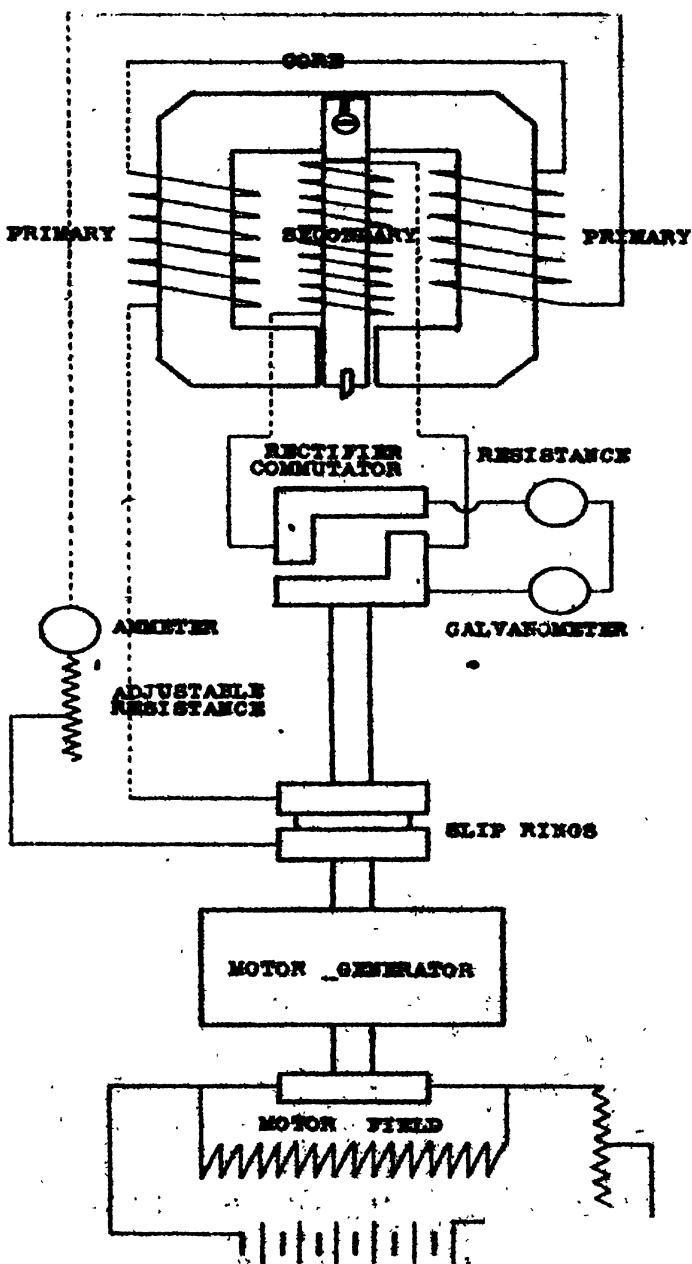RESISTANCE

SLIP RINGS

MOTOR — GENERATOR

MOTOR FIELD

Fig. 3.

The armature was pivoted as shewn, and held by hardened steel pins, and was easily removable. This enabled modification to be readily effected in the size of armature, gap, and windings.

Alternating current was supplied from a motor-generator set, and the current through the primary coils controlled by rheostat. A rectifying commutator was attached to the shaft of the alternator, and was included in the secondary circuit, the secondary current being read by a milli-voltmeter. Fig. 8 shows the detail of the connections.

The commutator at first gave considerable trouble, but with suitable carbon brushes and adjustable tension, it was found possible to considerably improve its action. To calibrate the instrument the method of obtaining small extensions by loading a wire was adopted. A No. 18 steel piano wire was used, about two metres in length, with suitable vernier attachment, and extensions were produced by suspending the wire vertically and applying direct loading. After calibration the wire was adjusted to a length of 44.25 ins., which gave an extension of $\frac{1}{1,000}$ in. for 1 lb. loading.

The extensometer was supported by a pair of similar wires, the armature being attached to the calibrated wire.

The milli-voltmeter used was a portable direct-reading deflection type galvanometer of the D'Arsonval pattern, by Siemens and Halske. Its resistance was 803 ohms and 1 div. = .0002 volts, and sensitiveness such that one scale division corresponded to a movement on the extensometer of $\frac{1}{240,000}$ in. The full scale of the galvanometer corresponded to a movement of 1.25×10^{-3} ins. For greater movement a resistance was placed in series with the galvanometer. A series of readings for calibration purposes is given in Table I. Fig. 4 shows

TABLE I.

Speed :—1,135 R.P.M.   Current :— 1 amp.
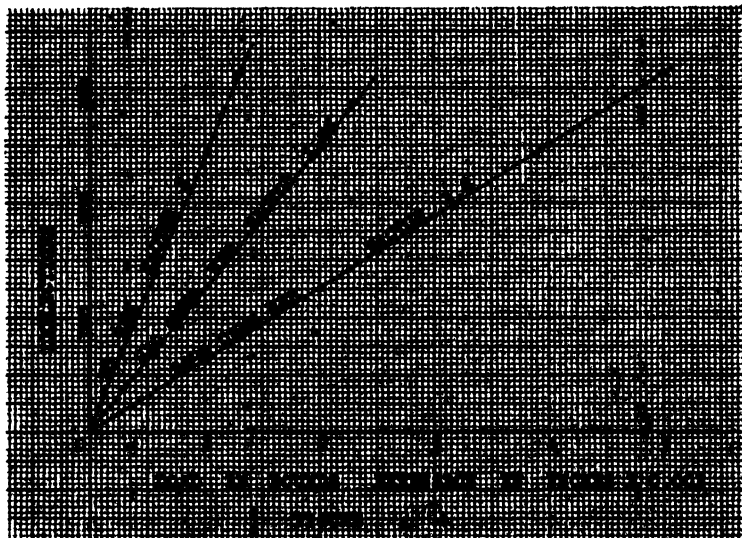
No Resistance.

Load in Grains.	Reading.		Deflection.	
0	8	5	0	3
1,000	45	41	37	33
2,000	80	80	72	72
3,000	111	111	103	103
4,000	147	153	139	145
5,000	184	190	176	182
6,000	216	219	208	211
7,000	253	252	244	244
8,000	283	285	275	277
9,000	319	..	311	

Resistance :—830 ohms.

Load in Grains.	Reading.		Deflection.	
0	9	8	0	1
2,000	45	45	36	36
4,000	82	78	73	69
6,000	114	115	105	106
8,000	150	149	141	140
10,000	185	184	176	175
12,000	220	219	211	210
14,000	254	257	245	248
16,000	293	..	284	..

Resistance :—2.490 ohms.

Load in Lbs.	Reading.		Deflection.	
0	15	15	0	0
1	77	77	62	62
2	138	140	123	125
3	200	202	185	187
4	263	264	248	249
5	326	..	311	..

the corresponding curves. The results show that for exten-
sions up to 5×10^{-8} inches the galvanometer readings are very
nearly proportional to the extensions.

Factors can be obtained for each resistance, which enable all deflections to be reduced in terms of deflections with no extra resistance in circuit.

Readings taken of a suitable deflection, with and without resistance, give the necessary factor. It was found that if load were left on the wire for some time the reading would vary somewhat. On this account, in obtaining further calibration curves, each reading recorded was the mean of five readings obtained by applying alternately load and no load. Tables 2

TABLE II.

Speed :—1,140 R.P.M.   Current :—1 amp.

Load in Lbs	Reading.	Accuracy.	Resistance.	Factor.	Reduced Deflection
0	0	Prob. Error %	0	0	0
0·25	58·8	4·4	,,	1	58·8
0·5	119·7	2·8	,,	,,	119 7
0·75	180 2	1·5	,,	,,	180·2
1	240·4	0·9	,,	,,	240·4
1·25	301·1	1·6	,,	,,	301·1
1 25	149·9	1·1	835	2·008	301·1
2	240·2	0·4	,,	,,	482·6
2·5	300	0 0	,,	,,	602·6
2·5	155·4	0·8	2,475	3·87	602·6
3·75	233·4	0·2	,,	,,	904·9
5	310·5	0 4	,,	,,	1,204
5	116·2	0 7	8,080	10·36	1,204
7	166·5	0·0	,,	,,	1,725
10	230·5	0 3	,,	,,	2,388
12	278·5	0·1	,,	,,	2 874
12	115 2	0 2	22,500	24·9	2.874
15	149 1	0·3	,,	,,	3,721
20	202·5	0·4	,,	,,	5,054
25	262·3	0·2	,,	,,	6,546
27	285	0 0	,,	,,	7.113

TABLE III.

Speed : —1,140 R.P.M.   Current :—1 amp.

Load in Lbs	Reading.	Accuracy.	Resistance.	Factor.	Reduced Deflection.
0	0	Prob. Error %	0	0	0
1	240·5	0 5	,,	1	240·5
2	240·1	0 8	835	2 0087	482·3
5	310·4	0 3	2,457	3·877	1,204
10	230·5	0 4	8,080	10·362	2,388
12	115·4	0 4	22,500	24·957	2.874
15	150·1	0·1	,,	,,	3,746
20	211	0·3	,,	,,	5,266
25	279·1	0 2	,,	,,	6,965
27	308	0·4	,,	,,	7,687

and 3 give the results for loads up to 25 lbs., representing a total extension of $\frac{1}{40}$ in. The readings in the last columns are reduced to the corresponding values with no extra resistance in the galvanometer circuit. Fig. 5 shows the results
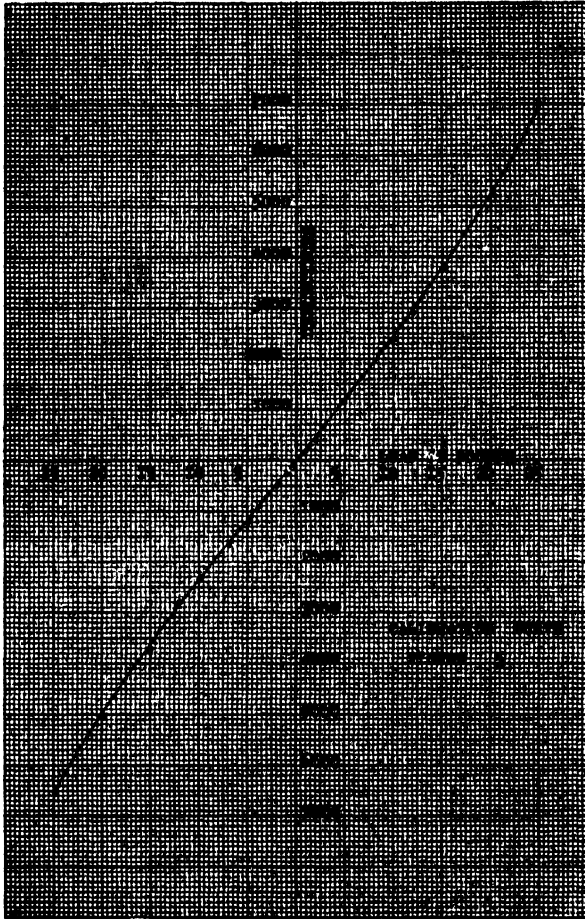
given in Tables 2 and 3. It appears that the deflections are very nearly proportional to the movement of the armature over a considerable portion of the range.
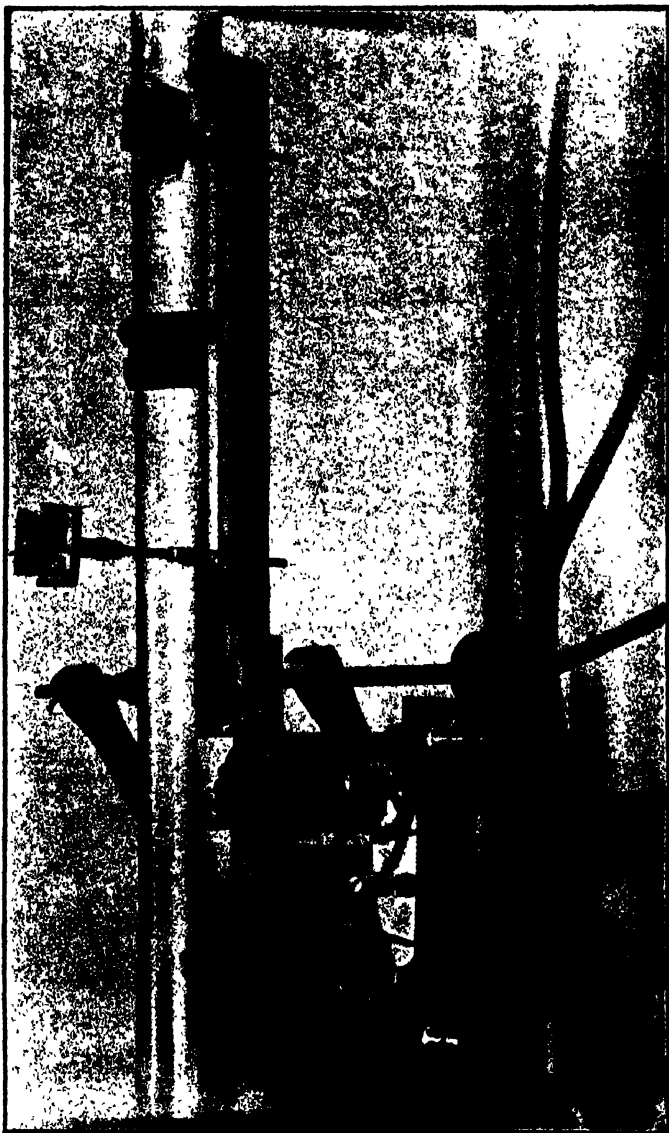
ELECTRO-MAGNETIC EXTENSOMETER

FIGURE 6

FIGURE 7

APPLICATION AS AN EXTENSOMETER.

The instrument was now adapted for application in the measurement of strains in ordinary test pieces in tension or compression. The distance over which these extensions are taken is usually about 8 inches. A hardened steel point is let into the end of the armature, and a steel knife edge, carried at the end of a hardened-steel rod rigidly attached to the core, forms the second contact. Fig. 6 shows the completed extensometer. A brass fork suitably milled out was attached to the core poles by bolts. To the end of this fork is attached the distance piece, which consisted of a hardened steel arm $\frac{1}{2}$ in. by $\frac{5}{32}$ in.. the end of which is bent at right-angles to form the grip. A "V" is cut in the end, and ground to form sharp edges. The distance between these edges and the steel pin on the armature when in its central position was made 20 centimetres.

The terminals were carried in a fibre strip attached to the core. The whole instrument was attached to the test piece by a spring clamp. Fig. 7 shows the extensometer attached to a test piece with a Marten's mirror extensometer having a 10 c.m. distance piece fitted underneath. To eliminate any bending of the test-piece, two extensometers should be used, one on each side of the specimen. However, for the preliminary experiment, the arrangement shown in Fig. 7 was used, it being assumed that any effect experienced over the 20 c.m. distance would be twice as great as that over the central 10 c.m. The test-piece was a standard Bessimer steel bar of sectional area, .6 square inches, and capable of being loaded to 6 tons. The specimen was held in a suitable testing machine; an initial load of half a ton was applied to bring the galvanometer pointer to zero.

The following tests were then carried out:—

(1) In order to ascertain if any slip occurred at the grip points, various loads were applied and then removed; the readings are given in Table 4, and agree within .4 per cent., showing that the method of attachment is efficient.

(2) Tests were made to compare the results obtained by the instrument with those obtained by the Marten's mirrors. The latter measured the extensions over 10 c.m., while the former was over 20 c.m. Table 5 shows the results for loads up to 1.25 tons. No extra resistance was placed in the galvanometer circuit. Consequently maximum sensitiveness was obtained. For a load of 1¼ tons the mirrors showed a deflection

TABLE IV.

Speed :— 1.140 R.P.M.   Current :— 1 amp.

| | No Resistance. | | 1000 ohms. | |
Load in Tons.	Reading.	Deflection.	Reading.	Deflection.
0	48	0	21	0
1	308	2 0	140	119
0	48	260	21	119
1	307	259	139	118
0	47	260	20	119
1	307	260	139	119
0	47	260	20	119
		Mean : 259·8		Mean : 118·8

| | 1,000 ohms. | | 5,000 ohms. | |
Load in Tons.	Reading	Deflection.	Reading.	Deflection
0	10	0	3 5	0
2·5	324	314	102	98·5
0	9	315	3 5	98·5
2 5	325	314	102·5	99
0	9·5	315·5	4	98 5
2·5	323	313·5	102 5	98·5
0	8	3 15	3·5	99
		Mean : 314 5		Mean : 98·7

TABLE V.

Speed : —1,140 R.P.M.   Current : → 1 amp.

No Resistance.

Load in Tons.	Mirrors.			Galvanometer.	
	Moving.	Fixed.	Deflection.	Reading.	Deflection.
0	0	0	0	13	0
0 25	2·0	0·1	1·9	46	58
0 5	4·0	0·2	3·8	111	124
0·75	5·9	0·2	5·7	178	191
1	7·9	0·2	7·7	244	257
1·25	9 8	0·2	9·6	312	325
1·175	9·0	0·2	8·8	302	315
1	7 6	0·2	7 4	268	281
0·75	5·6	0·2	5·4	194	207
0 5	3·6	0 2	3·4	125	138
0·25	1·7	0·1	1·6	53	66
0	0·2	0	0·2	21	8

of 9.6 over 10 c.m., corresponding to 19.2 over the distance 20 c.m. These readings are to 1/10 scale dimensions, so that 192 readable spaces are available. For the same load the galvanometer deflection is 325 divisions, and with the mirror scale provided, this gives 650 readable spaces. The sensitiveness of the magnetic extensometer is then 3.4 times that of the mirrors. However, the consistency and reliability of the instrument has so far not been sufficiently investigated to warrant one in finally accepting its readings. Thermal and mechanical effects have still to be investigated.

Fig. 8 shows the curves plotted from Table 5.
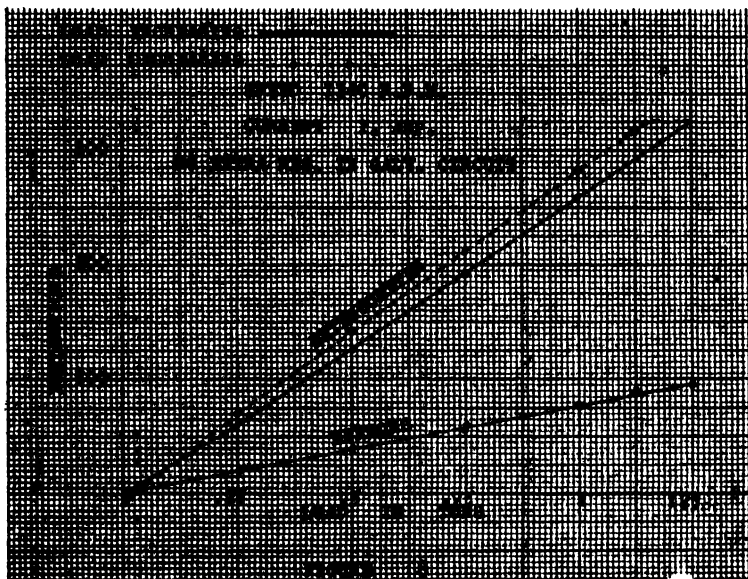
The reversal of load causes an apparent alteration in slope of the curve, which is only to be explained by some irregularity in the mechanism of the magnetic extensometer or its attachments. This point will be referred to later on, but it must be remembered that limits of reliability of the instrument will probably be determined by considerations other than purely electrical.

Test 3. With 5,000 ohms introduced into the galvanometer circuit, the sensitiveness is reduced and a larger range of load can be used.

Table 6 and Fig. 9 shew the results. In Fig. 9 the mean values for increasing and decreasing loads are plotted.

TABLE VI.

Speed : 1,140 R.P.M.   Current :— 1 amp.
Resistance :—5,000 ohms.

Load in Tone.	Mirrors.			Galvanometer.	
	Moving.	Fixed.	Deflection.	Reading.	Deflection.
0	0	0	0	20·5	0
0·5	4·1	0·4	3·7	4·5	16
1	8·0	0·7	7·3	15·5	36
1·5	11·9	0·8	11·1	35·5	56
2	15·7	0·8	14·9	55·5	76
2·5	19·4	0·7	18·7	76	96·5
3	23·2	0·6	22·6	97	117·5
3·5	27·0	0·5	26·5	118	138·5
4	30·9	0·4	30·5	140	160·5
4·5	34·7	0·3	34·4	161	181·5
5	38·3	0·3	38·0	182·5	203
4·75	36·1	0·3	35·8	176	196·5
4·5	34·1	0·3	33·8	165·5	188
4	30·4	0·3	30·1	144	164·5
3·5	26·7	0·4	26·3	121·5	142
3	22·8	0·4	22·4	99·5	120
2·5	19·0	0·5	18·5	78	98·5
2	15·1	0·6	14·5	56·5	76·5
1·5	11·3	0·6	10·7	36	56·5
1	7·6	0·5	7·1	16	36·5
0·5	3·9	0·3	3·6	4·5	16
0	0	0.1	0·1	24	3·5
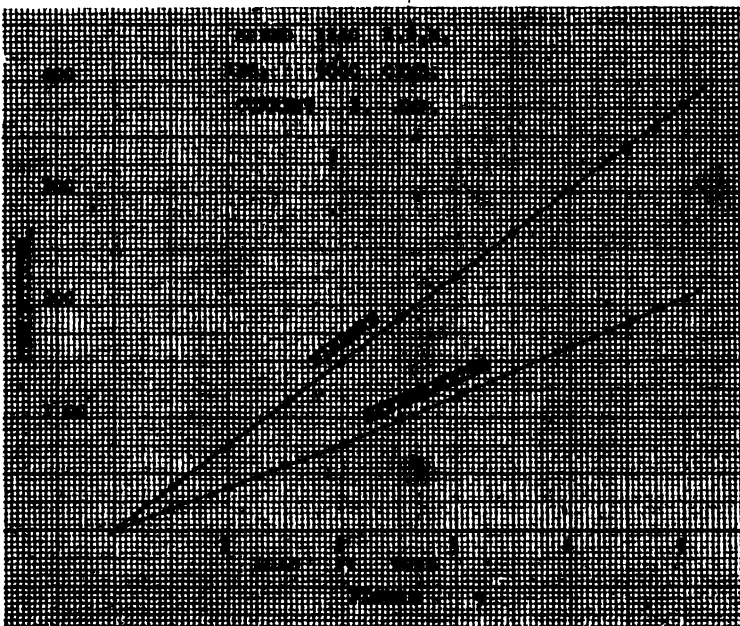
RECORDER   DIAGRAM.
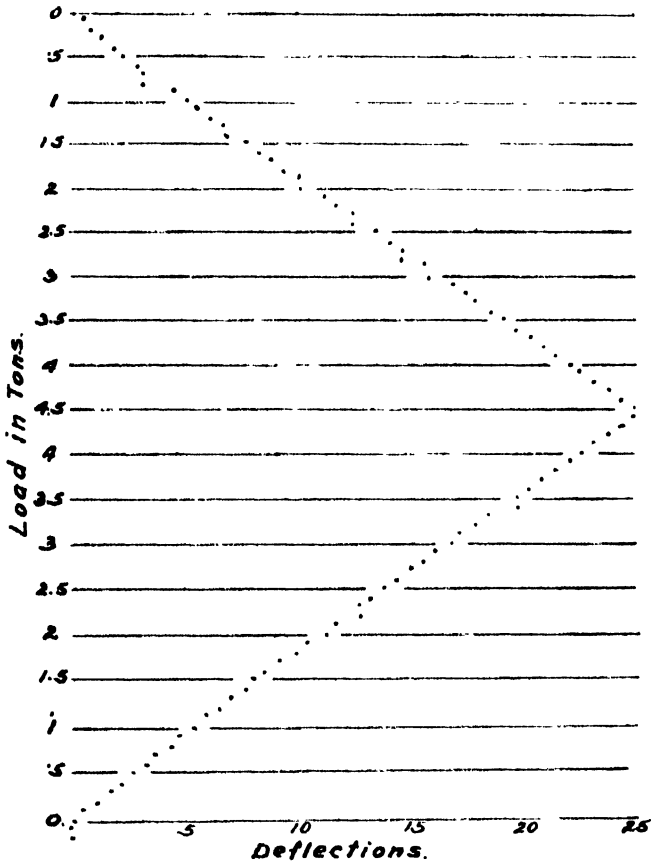

FIGURE   IO

Speed = 1140 R.P.M.   Current = 1 amp.

Resistance = 2800 ohms.

Test 4. To ascertain if a continuous record could be obtained, a Fery Thread Recorder was used in place of the galvanometer. Load was applied to the test piece at a uniform rate. Fig. 10 is a record taken by this instrument with 2,800 ohms in circuit. The load was applied at .1 tons every half-minute to 4.5 tons, and then decreased at the same rate. Similar discrepancies appear as remarked on previously in the case of the direct readings, but the test is sufficient to show that the instrument is adaptable for record purposes within certain limits.

Test 5. The effect of resistance in the galvanometer circuit is shown in Fig. 11; factors obtained by reading a given
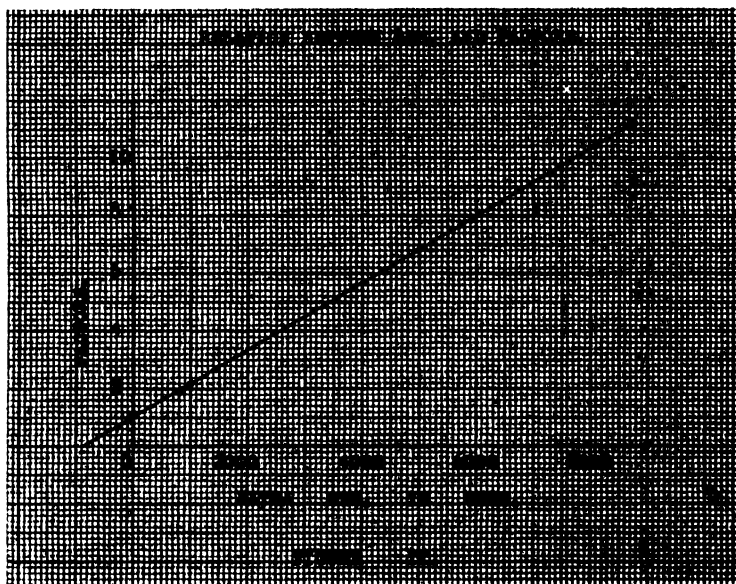
extension with and without resistance are plotted against resistance. This shows that deflections are approximately proportioned to the total resistance in the galvanometer circuit.

In the experiments so far described, the alternating current was derived from a 10 k.w. alternator driven by motor, with the rectifier attached to the shaft. The machine was much larger than was required, but enabled steady conditions in regard to frequency and current adjustment in the primary coils to be obtained.

As the actual amount of power required to operate the extensometer is not more than a few watts, attempts were made

at this stage to reduce the size of the generator used. Several attempts were made with very small machines, but all proved more or less unsatisfactory. To obtain reasonably steady running, it was found that the best results were obtained from a motor-generator set; rotary converters transferred irregularities from the D.C. to the A.C. side, and machines with double wound armatures, though satisfactory to a certain extent, were not found to afford all the advantages given by a set with distinct motor and generator.

An improved method for gripping the extensometer was developed by Mr. W. H. H. Gibson. The modifications in design to allow of the application of two instruments to the opposite side of a round test bar are shown in Fig. 13. The side
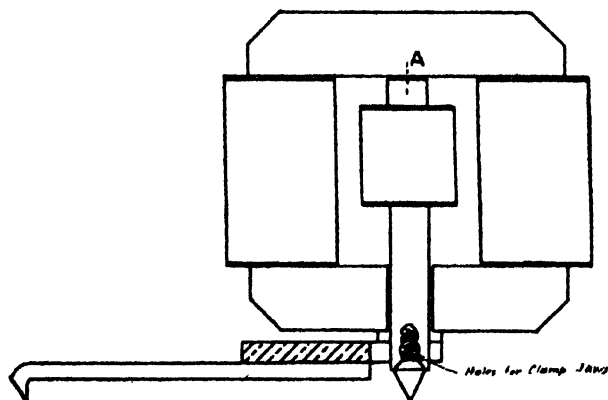
Arrangement of Distance-Piece &
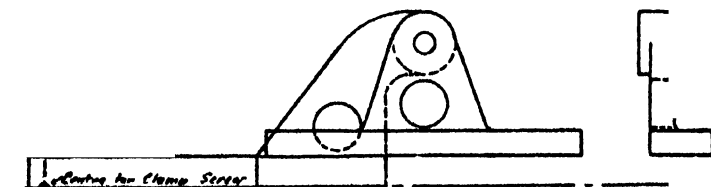
FIGURE 13.

brackets are brass castings. A brass cross-piece is attached to the bosses of the brackets, and passes under the instrument. A single distance piece is attached to the middle of the cross-piece by screws, and preferably dowelled in plates; each distance piece is intended to be permanently attached to its cross-piece, the whole being removed and another unit attached in its place

if it is desired to change the gauge length. The knife edge on the tongue is made from round steel screwed on the end, and provided with a conical shoulder, which is drawn up in a cored seating in the tongue to prevent movement relative to the tongue. For further security it might be brazed in place, but the above method has so far not proved unsatisfactory.
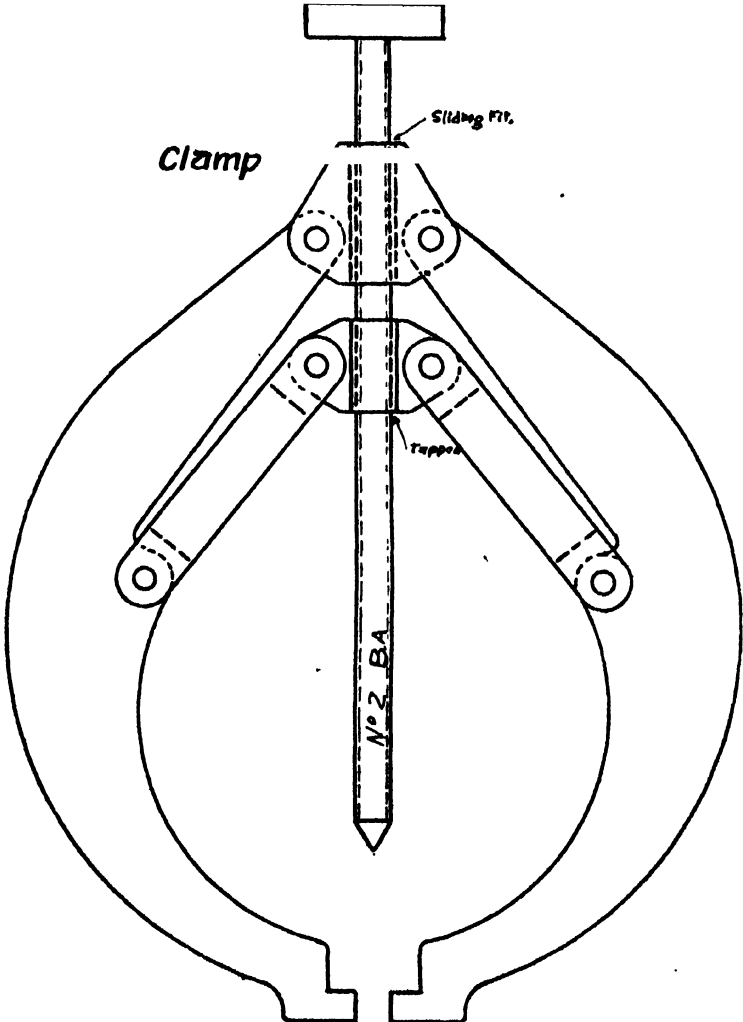

FIGURE 12.

The edge is necessarily ground after being fixed in place. As the other knife edge is ground on the end of the distance piece, it is not likely that there will be any movement.

A centre above the last-mentioned knife edge is intended to take the point of the clamp screw, while the jaws of the other clamp fit into holes in the protruding part of the tongue. The clamp is shown in Fig. 12. The jaws are designed to grip the tongue of one instrument while the screw presses on the distance piece of the other above the knife edge, a pair of clamps being used with a pair of extensometers.

The instruments are held firmly, and there is no load on the pivots. The clamps are designed to hold extensometers on round bars up to 2¼ inches diameter, and the jaws will open sufficiently to pass over such bars. For use with small bars the screw should be lined up accurately, and all pin joints must fit well. In a horizontal testing machine the extensometers should be mounted above and below the bar. The tongue of the instrument, as shown in Fig. 2. is held in position and pivoted by steel screws pressed hard into the core. This arrangement was used in the first place to enable the parts to be easily got at. It is proposed, however, in the final design to eliminate these screw pivots, and to hold the tongue in position, still giving it the necessary freedom of movement. by brazing a thin steel strip into slots cut into the tongue and core, as shown dotted at A in Fig. 13.

A difficulty which has to be met in the application of the extensometer is that even though great care be used in setting

EXTENSOMETER WITH COMPENSATOR.

FIGURE 14
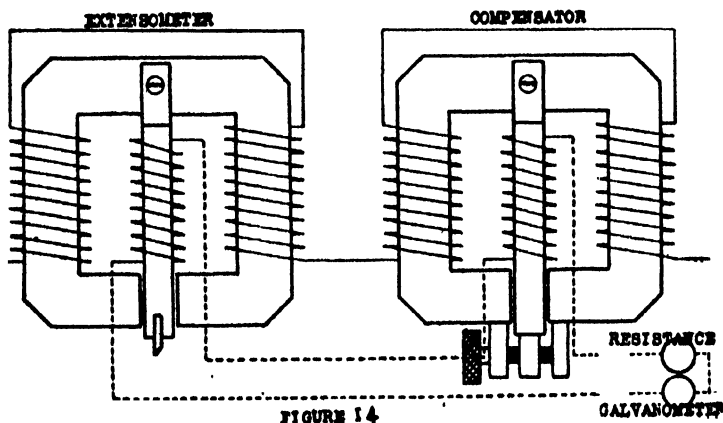
up the instrument on to gauge marks on the specimen, it will seldom be possible to so set it that the galvanometer reading initially will be zero.

To overcome this difficulty a second instrument, which we shall call a "compensator," similar to the extensometer, except that fewer turns are provided on the secondary winding on the tongue, and except that the tongue can be controlled by some simple mechanical means, was joined in circuit with the extensometer, as shown in Fig. 14.

Fig. 15 shows the compensator with its mechanical attachment. The primary coils of both instruments were joined in series and supplied with an alternating current of constant strength. The secondary coils of both instruments were similarly joined in series and connected to the rectifying commutator.

So long as the extensometer was set so that the tongue was in approximately a central position, movement of the tongue of the compensator, which was controlled by a screw gauge callipers, brought the galvanometer reading to zero.

The same result could no doubt be obtained by attaching a mechanical device to the grip furthest from the extensometer body, enabling a fine adjustment of the grip to be made. This arrangement would not be as convenient as the "compensator." There appears, however, a possibility that the E.M.F. in the compensator secondary winding may not always be in phase with the E.M.F. in the extensometer secondary for all positions of the tongue; this point needs further investigation. A point to which special attention should be called is. that the inductance of the primary circuit of the extensometer does not remain constant as the tongue is moved across the gap. The effect is to vary the phase difference between the primary current and the E.M.F. in the primary circuit. Consequently the position of the rectifier commutator must be varied with the movement of the tongue, if complete rectification is required. Complete rectification is, however, not essential. Moreover, it is possible to correct for this by the use of variable inductance in the primary circuit, instead of the variable resistance so far used; or to include in the primary circuit sufficient inductance to render the variation negligible. There is little doubt that in the past a considerable amount of the variation caused by this effect was attributed to faulty action of the rectifier. The shape of the calibration curve can be altered by adjustment of the position of the rectifier commutator; also by variation in shape of the pole-pieces or tongue.

As considerable difficulty was experienced from time to time in maintaining the rectifying commutator in satisfactory
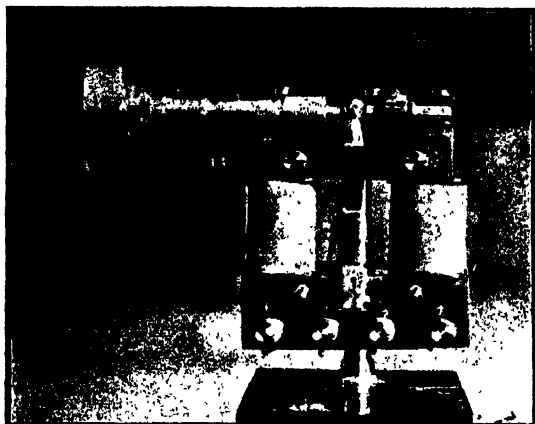
COMPENSATOR WITH MECHANICAL ADJUSTMENT

FIGURE 15

order, especially when made in the smaller sizes to attach to the smaller generators, methods were tried with the object of eliminating the rectifier and using A.C. instruments.

One method to which a considerable amount of attention was devoted was to employ an A.C. galvanometer on the principle of the Abraham or Sumpner galvanometer, as shewn in Fig. 16.
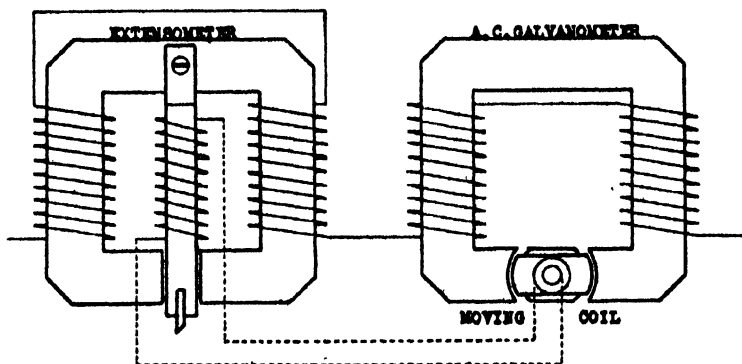
EXTENSOMETER WITH A.C. GALVANOMETER.

FIGURE 16

The primary coils of the extensometer were joined in series with the exciting coils of the Sumpner galvanometer.

The secondary coil of the extensometer was joined in series with the moving coil of the galvanometer.

The effects of change of frequency were, to a large extent, annulled; but a considerable decrease in sensitiveness was experienced.

Other methods tried were the Cohen barretter, thermo-galvanometer, telephone receiver, and vibration galvanometer.

None of these methods proved more satisfactory than the rectifying commutator with D.C. instruments.

However, our experience has been that rectifiers cannot always be relied upon over any but short periods of time, and even for short periods require care in design and operation.

An attempt is at present being made to construct a mercury rectifier, which it is thought will overcome some of the difficulties experienced with the metal commutator type. Preliminary experiments seem to indicate a possibility of success. At present this apparatus is under construction,

Although the development of the extensometer is still only in an experimental stage, it has been possible to proceed to a limited extent with some of its applications. Investigations upon the strains in the neighbourhood of riveted joints have been attempted, measuring over distances of one centimetre and less. For this purpose the extensometer is provided with two steel points, one let into the tongue, the other into the core, about one centimetre apart. The application to the measurement of strain in existing structures has also been developed to some extent. The application to a torsionmeter was undertaken by Messrs. P. E. Tandy, E. F. Campbell, and A. R. Edwards, and it has been shewn that the apparatus can be used for such a purpose. One special advantage offered by the magnetic extensometer, as compared with other forms, is that the readings need not be taken close to the apparatus. A number of such instruments could be fitted to various members of a structure, and the deflections, or continuous records for slowly-moving loads, could be taken at a distance. Other applications will, no doubt, suggest themselves.

We are indebted to Mr. Maclaren, mechanic to the Department, for the care with which he has constructed numerous pieces of apparatus used in the investigation.